Geochemical Significance of Biomarkers in Paleozoic Coals

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Abstract

Based on macroscopic fossils, the evolution of land plants is well documented. In contrast, knowledge on the biochemical evolution based on the geochemical characterisation of fossil plant material is poorly understood. The investigations of this thesis focus on the composition of extractable organic matter aiming to get insights into biochemical evolution. Additionally, the interdependency between oxygen containing compounds and the non functionalised aromatic hydrocarbons is investigated in detail. A set of 40 samples spanning the time range from Middle/Late Devonian to Permian has been investigated. Criteria for the selection of the samples were: (i) organic matter predominantly originating from terrestrial sources, (ii) having suffered little thermal alteration and (iii) only weak weathering. Due to the rarity of Paleozoic samples exhibiting all of these characteristics, the samples had to be sought from numerous locations worldwide. With the exception of two samples, they all belong to the Euramerian flora realm. The vitrinite reflectances of the samples range from 0.32 to 1.80% R_r. Most of them are coaly shales, though a few sediments and two fossils are included in the collection.

For the characterisation of compound classes and individual compounds, low molecular weight organic matter was extracted and separated into compound class fractions via liquid chromatography. Five of the gained fractions, the aliphatic hydrocarbons, the aromatic hydrocarbons, the low-polarity and middle-polarity NSO compounds and the acid fractions were investigated in detail. Individual compounds were identified and quantified applying gas chromatography (GC) for the aliphatic hydrocarbons and gas chromatography-mass spectrometry (GC-MS) for the other four compound class fractions.

Aliphatic hydrocarbons were minor contributors to the extractable organic matter for most of the samples and yielded little biogenic information. They served to estimate the thermal maturity and the redox potential of the samples. The absence of long chain *n*-alkanes in most of the immature samples, indicates that cuticular waxes are not an unambiguous characteristic of vascular plants in the Paleozoic.

Among the investigated compound classes, alkyldibenzofurans, alkylphenylnaphthalenes and benzo[*b*]naphthofurans were assigned to be terrestrial biomarkers. While variations in relative amounts of alkyldibenzofurans point to different origins of individual isomers, isomers of alkylphenylnaphthalenes and benzo[*b*]naphthofurans seem to originate from the same sources. It is suggested in this thesis that alkylphenylnaphthalenes may originate from lignans and that benzo[*b*]naphthofurans are condensation products of an ubiquitous terrestrial source.

Alkylnaphthalenes and -phenanthrenes are predominant in all investigated samples, this being typical for terrestrial organic matter of the investigated maturity range. Isomers of alkylphenanthrenes showed weaker correlation than isomers of alkylnaphthalenes. It is therefore suggested, that alkylnaphthalenes are formed earlier than alkylphenanthrenes with respect to thermal stress and that isomerisation reactions of alkylnaphthalenes therefore proceed prior to those of alkylphenanthrenes. The biogenic significance of individual alkylnaphthalenes and -phenanthrenes is rather complex and is discussed in detail. Based on the data of this thesis the significance of 1,2,7-trimethylnaphthalene as a marker of angiosperms is questionable. In contrast 1,2,8-trimethylphenanthrene could be identified as a compound showing high variations in relative amounts. Thus, it is suggested that the compound originates from tetracyclic triterpenoids of the dammarane type or from plant steroids.

Functionalised compounds based on the naphthalene and phenanthrene skeleton are also highly abundant in the low-polarity NSO compound fraction and the acid fraction, this being more pronounced for compounds of the naphthalene type. Both, aldehydes and ketones as well as carboxylic acids strongly correspond to their non-functionalised aromatic counterparts. This strongly indicates that functionalised compounds are formed from the aromatic hydrocarbons via oxidation within the investigated maturity range. This is supposed to occur under mild conditions in the case of aldehydes and ketones, while the formation of carboxylic acids is probably forced under thermal stress. By analogy methylfluorenes and methylfluoren-9-ones show strong correlation indicating that alkylfluorenes are easily oxidised in sediments, too.

The lowest overall yields of extractable compounds were obtained for the middle-polarity NSO-compound fractions containing alcohols and phenols. This observation was attributed to their depleted thermal stability with regard to the maturity range of the investigated samples. The presence of isoborneol, borneol, fenchyl alcohol, camphor, verbenone, menthol, carvacrol, thymol and menthone in many immature samples expanding the period from the Middle/Late Devonian to Permian ages, however, is observed for the first time. This is remarkable due to the

fact that some of these compounds are strained and their presence probably is of great significance, pointing to the capacity of these ancient terrestrial plants to synthesize these monoterpenes.

Kurzfassung

Die Evolution der Landpflanzen ist durch fossile Überlieferung auf der makroskopischen Ebene gut dokumentiert. Im Gegensatz dazu ist die zugrundeliegende biochemische Evolution im Hinblick auf die geochemische Charakterisierung fossilen Pflanzenmaterials so gut wie nicht erforscht. Diese Arbeit analysiert extrahierbares organisches Material mit dem Ziel, Einblicke in die biochemische Evolution der Landpflanzen zu gewinnen. Zusätzlich wird der Zusammenhang zwischen sauerstoffhaltigen Verbindungen und den nicht funktionalisierten aromatischen Kohlenwasserstoffen detailliert untersucht. Es wurden 40 Proben des Zeitraumes Mittleres/Oberes Devon bis Perm analysiert. Kriterien für die Auswahl der Proben waren: das organische Material sollte (i) hauptsächlich terrestrischen Ursprungs sein, (ii) nur geringe thermische Überprägung erfahren haben und (iii) der Witterung möglichst wenig ausgesetzt gewesen sein. Aufgrund der geringen Anzahl an Paläozoischen Proben, die diese Eigenschaften auf sich vereinigen, stammen die Proben von zahlreichen Orten weltweit. Bis auf zwei Proben gehören jedoch alle zur Euramerianischen Florenprovinz. Die Vitrinitreflektion der Proben liegt zwischen 0,32 und 1,80% R_r. Die meisten sind kohlige Tonsteine, außerdem sind einige Sedimente und zwei Fossilien Bestandteil der Probenserie.

Zur Charakterisierung der Verbindungsklassen und spezifischer Verbindungen wurde das niedermolekulare organische Material extrahiert und mittels Flüssigkeitschromatographie in Verbindungsklassenfraktionen separiert. Unter den hier gewonnenen Fraktionen wurden fünf, die aliphatischen und aromatischen Kohlenwasserstoffe, die Fraktionen der niederpolaren und mittelpolaren Heteroverbindungen sowie die der Säurefraktion detailliert untersucht. Einzelverbindungen wurden für die aliphatischen Kohlenwasserstoffe mittels Gaschromatographie (GC) und für die übrigen vier Verbindungsklassen mittels Gaschromatographie-Massenspektrometrie (GC-MS) identifiziert und quantifiziert.

Aliphatische Kohlenwasserstoffe machten einen geringen Anteil des extrahierbaren organischen Materials aus und lieferten für den Großteil der Proben wenig biogene Information. Sie dienten dazu, die thermische Reife und das Redoxpotential

der Proben zu bestimmen. Das Fehlen von langkettigen *n*-Alkanen in vielen der unreifen Proben weist jedoch darauf hin, daß Kutikularwachse nicht notwendigerweise von Gefäßpflanzen des Paläozoikums produziert wurden.

Alkylnaphthaline und -phenanthrene dominieren in allen Proben. Dies ist typisch für terrestrisches organisches Material des untersuchten Reifeintervalls. Die Verteilung der Alkylphenanthrene korreliert schwächer als die der Alkylnaphthaline. Dies wird darauf zurückgeführt, daß durch die thermische Reifung Alkylnaphthaline vor Alkylphenanthrenen entstehen und daß ihre Isomerisierung dementsprechend früher einsetzt. Die biogene Signifikanz spezifischer Alkylnaphthaline und -phenanthrene ist komplex und wird detailliert diskutiert. Aufgrund der Ergebnisse dieser Arbeit ist davon auszugehen, daß 1,2,7-Trimethylnaphthalin nur eingeschränkt als Angiospermenmarker genutzt werden sollte. Bei 1,2,8-Trimethylnaphthalin handelt es sich hingegen wahrscheinlich um einen Biomarker, der von tetracyclischen Triterpenen des Dammarane-Types oder von Pflanzensteroiden abstammen könnte.

Funktionalisierte Verbindungen des Naphthalin- und Phenanthrentypes sind außerdem wichtige Bestandteile der niederpolaren Heterokomponenten und der Säurefraktion. Dieser Befund ist bei den Verbindungen, die auf dem Naphthalingerüst basieren, besonders ausgeprägt. Sowohl Aldehyde und Ketone als auch Karbonsäuren korrelieren stark mit den entsprechenden nichtfunktionalisierten aromatischen Verbindungen. Dies läßt stark vermuten, daß die funktionalisierten Verbindungen für das untersuchte Reifeintervall mittels Oxidation aus den nicht funktionalisierten aromatischen Kohlenwasserstoffen gebildet wurden. Dies geschieht für Aldehyde und Ketone unter milden Bedingungen, während die Bildung der Karbonsäuren durch thermische Reifung begünstigt wird. Analog hierzu zeigen Methylfluorene und Methylfluoren-9-one eine starke Abhängigkeit. Das weist daraufhin, daß Alkylfluorene in Sedimenten bevorzugt oxidiert werden.

Die mittelpolaren Heteroverbindungen, d.h. die Fraktion der Alkohole und Phenole, bilden die Fraktion mit der geringsten Ausbeute. Dies wird auf die geringe thermische Stabilität dieser Verbindungen im untersuchten Reifeinterval zurückgeführt. Das Vorhandensein von Isoborneol, Borneol, Fenchylalkohol, Kampher, Verbenon, Menthol, Carvacrol, Thymol und Menthon in vielen unreifen Proben des gesamten untersuchten Zeitintervalls wird in dieser Arbeit erstmals dokumentiert. Dies ist insbesondere bemerkenswert, da es sich bei einigen um gespannte Verbindungen handelt. Ihr Auftreten in den untersuchten Proben zeigt, daß die Landpflanzen des Paläozoikums bereits die Fähigkeit besaßen, diese Verbindungen zu synthetisieren.

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List of Abbreviations

ATR	Aquatic/ Terrigenous Ratio of Hydrocarbons
BP	Before Present
CO_2	Carbondioxide
CPI	Carbon Preference Index
DBF	Dibenzofuran
DNR	Dimethyl-Naphthalene-Ratio
DPR	Dimethyl-Phenanthrene-Ratio
EI	Electron Ionisation
eV	Electron Volt
FID	Flame Ionisation Detector
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectrometry
HC	Hydrocarbons
HI	Hydrogen Index (mg HC/g TOC)
HHI	HomoHopaneIndex
H-MPLC	Hetero-Medium Pressure Liquid Chromatography
i.d.	Internal Diameter
m/z	Mass/Charge
MPLC	Medium Pressure Liquid Chromatography
MPI	Methyl-Phenanthrene-Index
n.d.	not detected or unreliable
NSO	Nitrogen, Sulphur and Oxygen
OEP	Odd-over-Even Predominance
OI	Oxygen Index (mg CO_2/TOC)
OM	Organic Matter
R_c	Calculated Vitrinite Reflectance, extrapolated from a geochemical parameter
R_r	Vitrinite Reflectance
SO_3	Sulphurtrioxide
TC	Total Carbon
TOC	Total Organic Carbon
TS	Total Sulphur

1 Introduction

1.1 Evolution of the System Earth during the Late Paleozoic

Evolution is an ongoing process. However, especially the Late Paleozoic (354-251.4 Ma BP) is characterised as the period when terrestrial life evolved and differentiated most significantly. The two periods attributed to the Late Paleozoic are the Carboniferous (354-292 Ma BP) and the Permian (292-251.4 Ma BP). The era is preceded by the Devonian (Middle Paleozoic, 417-354 Ma BP) and followed by the Triassic (Mesozoic, 250-205.1 Ma BP).

At the beginning of the Paleozoic (545 Ma BP), life of fauna and flora is limited to the sea. While marine life did not differ strongly since the Devonian, terrestrial environments until the end of the Paleozoic were subject to extreme changes basically due to the evolution of land plants. Although fossil spores from the Middle Ordovician (Early Paleozoic, 495-440 Ma BP) indicate the existence of land plants at this time (Gray, 1993), a significant colonization of land masses by plants probably has not occurred until the Middle Paleozoic (440-354 Ma BP). The inhabitance of terrestrial environments by plants is an important evolutionary challenge as it is the beginning of life for both fauna and flora beneath the sea (Kenrick and Crane, 1997). After early colonization, significant diversification and expansion of land plants is attributed to the Late Paleozoic. While especially the Carboniferous is characterised by the evolution of new animal and plant groups which in turn influenced the deposition processes of sediments, the Permian is the period at whose end the biggest mass extinction took place and many of the evolved

fauna and flora disappeared again. Although there is common agreement on the approximate evolutionary steps of land plants, detailed knowledge is limited.

In any case the transition of life from sea to land means a drastic change in life style (Gray and Shear, 1992). To survive and expand on land, plants required significant evolutionary adaption. The generation of a transport system for nutrient and water supply for example is necessary due to the different environmental conditions on land in comparison to the sea i.e. the presence of an atmosphere in general.

The early evolution of land plants is also influenced by several changing environmental factors which to different degrees show an interdependency to the evolution of land plants. Indeed environmental conditions are significantly influenced by the expansion and evolution of land plants. Elevated photosynthesis and therefore liberation of oxygen for example strongly influences the composition of the atmosphere, while enhanced production of biomass changes composition of land masses and in turn results in elevated fluxes of these sedimented biomasses into sea. In turn the evolution of land plants for example the composition of lignin is influenced by the oxygen contents of the atmosphere. Tectonic movements in contrast show weaker dependence on the evolution of plants. Tectonics however is an important factor with regard to the first occurrence of land plants, due to its influence on the position of land masses. The inhabitance of land masses by plants began at low latitudes. Due to their influence on the evolution of early land plants, both tectonic and climatic conditions of the Paleozoic have to be regarded.

The significant inhabitance of terrestrial environments probably began in the Silurian (Middle Paleozoic, 440-417 Ma BP) and was predominantly restricted to land masses that were located in temperate to subtropical regions. At this time, the supercontinent Gondwana expanded from the South Pole to the equator and made up to 70% of the Earths continental area (Scotese *et al.*, 1999). At the same time different parts of Gondwana experienced polar, temperate, subtropical and equatorial climates. Baltica and Greenland, but also the north eastern part of Gondwana, i.e. Australia then were located at the equator. In the Early Devonian Euramerica had formed at low latitudes, whereas the center of Gondwana had moved northwards. Paleozoic forests inhabited Euramerica. Whereas at the beginning of the Late Paleozoic in the Early Carboniferous continents had

generally drifted northwards, the Late Carboniferous was characterised by the formation of Pangea due to the collision of the southern parts of Gondwana and the continents that would later form North America and Europe (Euramerica) (Ross, 1999). In the Late Permian Pangea and Gondwana formed a huge continent expanding from the South Pole to the North Pole. Whereas Australia had separated from Gondwana during the Early Carboniferous, Siberia, North and South China already evolved separately from the Middle Silurian (Scotese, 2000). While the evolution of land plants probably began uniform the, the separation of individual land masses may be important due to the formation of separate flora realms.

Moreover latitudal movements of continents result in climate changes for certain land masses, and therefore influence their settlement by land plants. Nevertheless the changes in climate are not restricted to latitudal movements of land masses only. From Middle to Late Paleozoic global climate changed from hot house to ice house conditions and ended in hot house conditions again. Hot house periods are characterised by the fact that none of the poles is permanently covered with ice and strong seasonal cooling in general is rare. In contrast during ice house periods both poles are permanently covered with ice. Mean temperatures are 12-14°C for ice house periods, while the average temperature of hot house periods lies around 18-22°C. A change from ice house to hot house conditions occurred from Late Ordovician to earliest Silurian and was followed by a period of global warming expanding from the Silurian to the Middle Devonian. A decrease in global climate during the Middle/Late Devonian results in predominantly ice house conditions during the Carboniferous and the Permian. At the end of the Permian and the beginning of the Mesozoic temperatures raised again. The change in climate at the end of the Permian is supposed to have a significant influence on the mass extinction.

Floral changes are known to depend on climatic variations (Kerp, 1996). Additionally global average temperatures significantly influences terrestrial areas and sedimentation. Warm periods normally result in transgressions while sea regresses when polar caps are covered with permanent ice. The flooding of terrestrial environments in times of transgressions results in a depletion of terrestrial land masses and an increase of marine input into the sedimentary organic matter. Due to

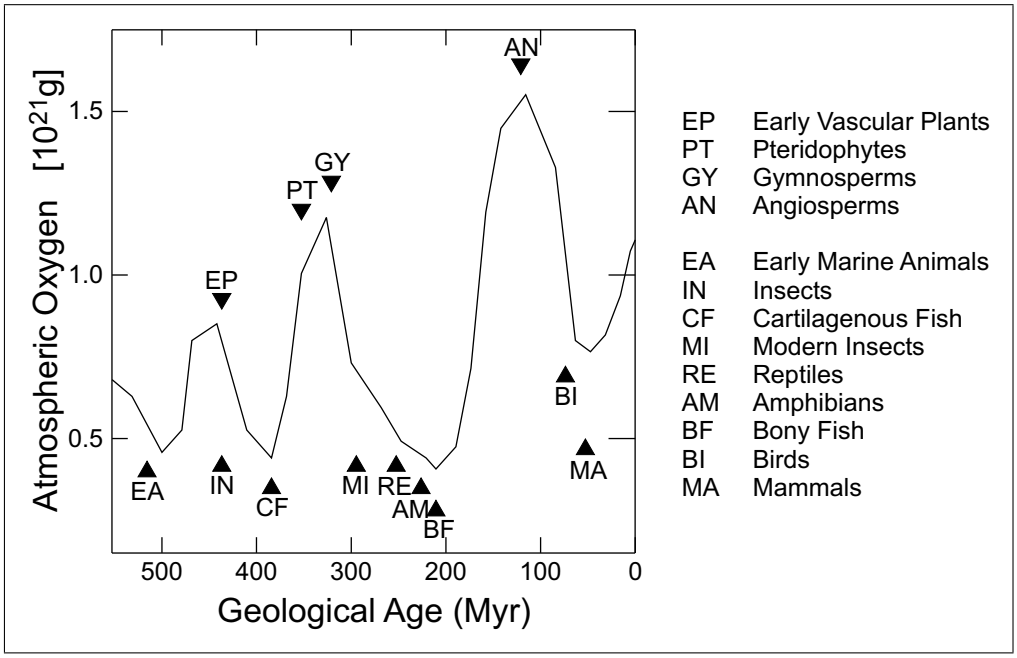

Figure 1.1: Correlation between the oxygen content of the atmosphere and evolution of land plants and animals (Gottlieb, 1989)

transgressions depositional environments become marine, while in warm periods terrestrial depositional environment show little input of marine organic matter.

Although climatic conditions and therefore the mean temperatures on Earth are influenced by several factors, for example the solar radiation and the biosphere, the composition of the atmosphere probably plays the most important role. While Milankowitch cycles describe the orbit of the Earth around the sun and therefore help to assess solar radiation, mean temperatures on Earth would be low without the atmospheres capacity to retain heat (Barnes, 1999). This does especially account for the contents of CO_2 in the atmosphere. High proportions of CO_2 support hot house conditions. While the amounts of nitrogen (N_2) are assumed to have been relatively constant during the Paleozoic, partial pressures of oxygen (O_2) and carbon dioxide (CO_2) have varied more significantly (Graham *et al.*, 1995). Crowley and Baum (1995) found a positive correlation between CO_2 contents of the atmosphere and changes in climate, and assumed, that diversification of life may have depressed CO_2 levels. The significant decrease of CO_2 levels is supposed to have started in the Silurian/End-Ordovician, reaching its minimum in the Carbonifer-

ous/Permian period (Graham *et al.*, 1995). This decrease of CO_2 is accompanied by an increase of oxygen partial pressure (Fig. 1.1). It is most likely that the CO_2 depression can be attributed to the evolution of land plants and their expansion, i.e. the significant increase of biodiversity in Late Paleozoic times (Rothman, 2001). Indeed an emergence of plants correlates with times when oxygen shows depleted levels, compared to CO_2 (Fig. 1.1), while their diversification coincides with elevated oxygen levels (Gottlieb, 1989). Conversion of CO_2 to organic matter results from photosynthesis. The CO_2 required for photosynthesis in land plants is taken from the atmosphere. The consumption of CO_2 is controlled by diffusion. Animals on the other hand emerged at times of oxygen maxima (Fig. 1.1). This is due to the fact, that their respiration requires oxygen. Mass extinctions correspond to times when oxygen levels have been low, while atmospheric oxygen contents are not necessarily the causes for these extinctions (Gottlieb, 1989).

1.2 Origin and Evolution of Land Plants

Earliest land plants belong to the groups of bryophytes (mosses, hornworts and liverworts) and tracheophytes (lycopyds, horsetails, ferns and seed plants). The colonization of land masses by plants probably took place in low-lying freshwater or marginal marine environments. Most of the landmasses where land plants evolved were located between 30° and 60° of the paleoequator and offered tropical or subtropical climate, abundant sunlight, frequent dry periods and poor soil formation (Gensel and Andrews, 1987).

Earliest inhabitants of terrestrial environments probably have been bacteria, algae, lichens and fungi (Kenrick and Crane, 1997). These organisms played a significant role within the conversion of inorganic soils, especially with respect to the release of nutrients. They therefore developed important features that facilitated the inhabitance of terrestrial environments (Gray and Shear, 1992).

The ancestors of early land plants are not certainly known. It is presumable that both groups, the bryophytes and the tracheophytes have an aquatic origin. However they differ notably and it is most likely that they therefore have an indepen-

dent algal origin (Strickberger, 1996). Their similarities respecting this hypothesis then are not the product of an homology but a parallel evolution (Strickberger, 1996). It is commonly presumed that early tracheophytes evolved from charophytes i.e. green algae, which share many important characteristics, for example the capacity to produce sporopollenin, cutin, phenolic compounds and the glycolate oxidase pathway (Graham, 1985). The question which plant has been the earliest land plant is contradictory. Qiu *et al.* (1998) suggested liverworts to be the earliest land plants due to the fact that they miss some traits typical for other land plants. The uncertainty results from the fact that earliest land plants left no recognisable fossils. Whereas spores have already been discovered in Middle Ordovician deposits, megafossils attributed to plants can be dated back to the Silurian, only (Gray and Shear, 1992; Gray, 1993). These fossils of vascular plants belong to the genus of *Cooksonia* which reached heights of only few centimeters, showed no differentiation into steams and leaves and was characterised by the absence of true roots. These early vascular land plants probably were short lived, partly reflecting the fact that their capability was limited to primary growth (Edwards and Feeham, 1980; Gensel and Andrews, 1987). Vascular plants, which became established during Silurian times, diversified rapidly and outnumbered the non vascular plants by the end of the Devonian (Gensel and Andrews, 1987).

Significant diversification of early land plants occurred during the Devonian. While modern bryophytes still are predominantly limited to moist habitats, tracheophytes developed vascular tissues. The so-called xylem and phloem offers the opportunity to circulate water and nutrients. These features helped tracheophytes to adapt to widely different habitats (Gray and Shear, 1992).

Seed plants i.e. gymnosperms evolved during the Carboniferous and the Permian (Hart, 1987; Kerp, 1996). The evolution of heterospority, distinguishing seed plants had already proceeded in the Late Devonian (Gensel and Andrews, 1987). Tracheophytes, in particular horsetails and ferns probably are the ancestors of seed plants (Pryer *et al.*, 2001). Cycads, ginkgoales and conifers are attributed to gymnosperms (Fig. 1.2), the classification of Gnetales in contrast is contradictory (Bowe *et al.*, 2000; Chaw *et al.*, 2000; Schmidt and Schneider-Poetsch, 2002). While Schmidt and Schneider-Poetsch (2002) found that Gnetales are closest to

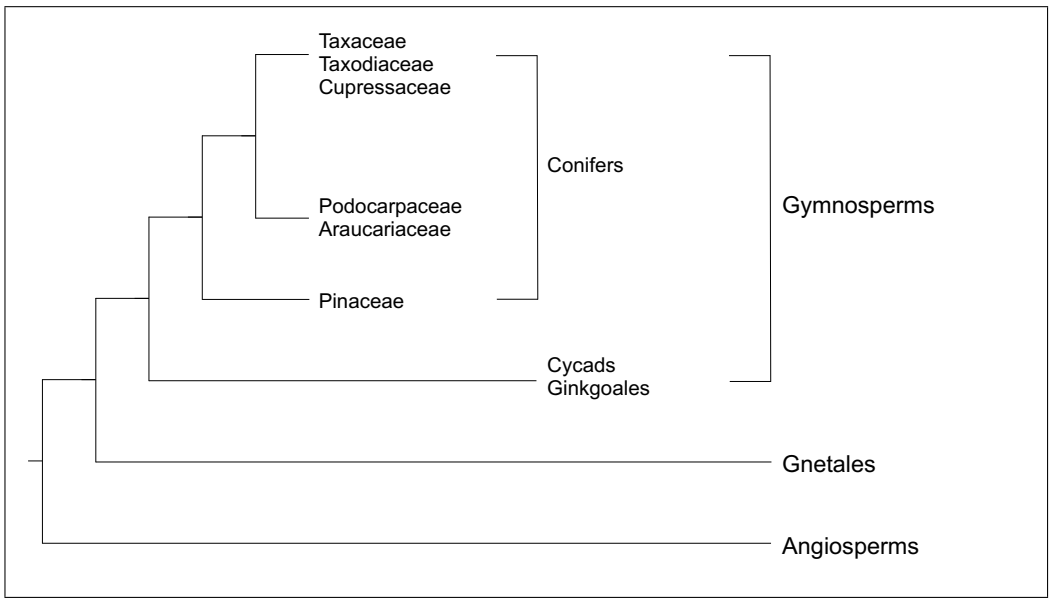

Figure 1.2: Relationship of seed plants and Gnetales according to Schmidt and Schneider-Poetsch (2002); in contrast Chaw *et al.* (2000) found Gnetales to be strongly related to Pinaceae

angiosperms (Fig. 1.2), Bowe *et al.* (2000); Chaw *et al.* (2000) found Gnetales to be monophyletic to conifers and to be a sister group to Pinaceae. Cycads and thereafter ginkgoales were the first gymnosperms to separate. Among the conifers it is generally accepted that Pinaceae were the first to separate (Hart, 1987; Bowe *et al.*, 2000; Chaw *et al.*, 2000; Schmidt and Schneider-Poetsch, 2002). The question of the phylogeny of Gnetales is important due to the fact, that they normally are regarded to be the ancestors of angiosperms. In contrast many of the recent studies cited above indicate, that the separation of angiosperms already occurred in the Late Paleozoic due to Gnetales showing a stronger relation to conifers and especially Pinaceae than to angiosperms.

At the end of the Paleozoic most families of the plant kingdom had evolved. Post-Paleozoic periods are characterised by a significant diversification and expansion of angiosperms. Fossils of angiosperms can be dated back to the Upper Cretaceous, whereas DNA-analysis of modern angiosperms indeed indicate that evolutionary specification related to their formation took place already during the Carboniferous (Martin *et al.*, 1989).

1.2.1 Evolution of Morphology and Secondary Metabolites

The adaptation of plants to terrestrial environments required several developments. These changes strongly affected the morphology of early land plants. They developed:

- waxy outer coatings, or cuticles to prevent the loss of water by cell surface evaporation,
- chemical mechanisms to protect plants from destructive influences of UV-radiation,
- stomata (pores) for gas exchange with the atmosphere,
- a system to transport water and nutrients,
- characteristical reproductive features (gametophytes and sporophytes) adapted to land.

In addition to be successful in terrestrial environments, plants evolved progressive differentiation into specialised parts, i.e stems, roots and leaves (Gensel and Andrews, 1987). The development of roots and stems enabled the vertical growth of plants. Vertical growth indeed is a characteristic of land plants, probably stimulated by the competition for sun light (Kenrick and Crane, 1997). Leaves became the places where photosynthesis is carried out. All listed features are characteristic for land plants and distinguish them from their likely aquatic ancestors.

These listed macro- and microscopical steps of evolution have been accompanied by the biochemical evolution of plant constituents. Although earliest findings of spores due to the preservation by sporopollenin coatings were attributed to earliest land plants, the capacity to produce sporopollenin is also due to living charophycean algae. Lignin, on the other hand, characterises vascular plants. Tracheophytes contain xylem which consists of lignin. Xylem is generally absent in bryophytes (Gray and Shear, 1992). The enhanced resistance of lignin against biotic and abiotic degradation may be an important factor for the formation of fossils (Gray and Shear, 1992). Another important constituent of land plants are

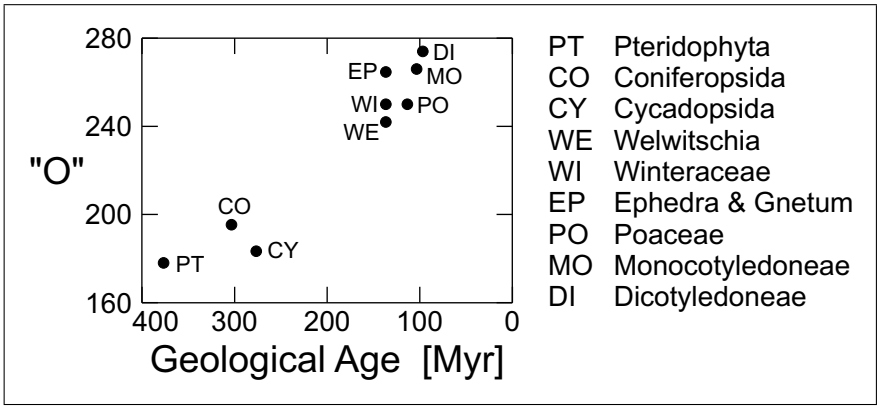

Figure 1.3: Correlation between the oxygen content of lignins and geological age (Gottlieb, 1989)

cuticles which protect them from evaporation. Cuticels consist of macromolecular (cutine, cutane) and low molecular (long-chain alkanes, ketones, alcohols, fatty acids and wax esters) constituents. Low molecular compounds in general fulfil various functions and are essential for terrestrial life. Pigments for example protect plants from UV radiation, allelochemicals act as defense against predators and antioxidants are important to prevent abiotic oxidation.

While lignins are the most abundant, flavonoids are the most widespread materials of terrestrial plants, except carbohydrates. An increase of the oxygen content of lignin has been observed with progressive evolution (Fig. 1.3). The oxygen content of lignin derived from angiosperms for example is higher than for gymnosperms (Gottlieb, 1989). This does also account for flavonoids (Fig. 1.4). With progressive evolution they show an enhanced chemical functionalisation, accompanied especially by an increase of oxygen contents (Gottlieb, 1989).

The importance of atmospheric oxygen has been mentioned previously. Although it does not seem to act directly within molecular evolution, an enhanced availability of oxygen probably triggers the evolution of enzymatic protective devices (Gottlieb, 1989). In general the morphological evolution is characterised by a progressive increase of the oxygen content of secondary metabolites (Gottlieb, 1989).

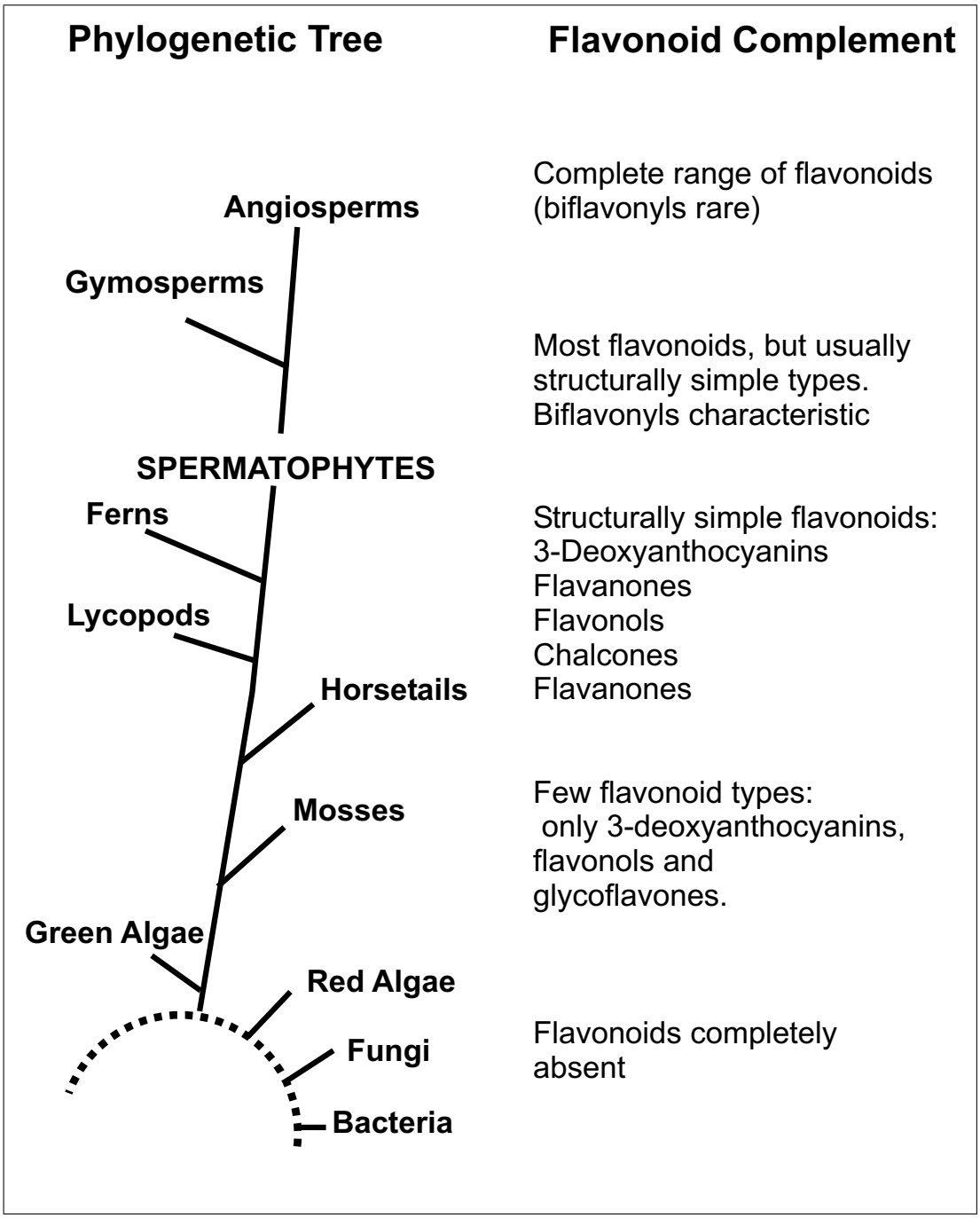

Figure 1.4: Evolution of flavonoids (Harborne, 1973)

1.2.2 Flora Realms in the Late Paleozoic

A problem considering the evolution of plants is the formation of distinguished flora assemblages (Chaloner and Meyen, 1973; Raymond *et al.*, 1985; Scott and Galtier, 1996). This diversification of flora assemblages is due to the separation of land masses in general but also to the formation of local communities where related plants adapt to different environments. Investigations on the formation of different flora provinces often are contradictory (Scott and Galtier, 1996). Plants from different regions but same ages may be considered to originate from different ages when viewing them outside their geological context (Scott and Galtier, 1996). Additionally relationship may not be recognisable when viewing the morphology of fossils only. For angiosperms it is known, that they possess different leaf shapes due to different habitats (Raymond *et al.*, 1985). Another important factor is the magnitude of preservation. The original composition of flora realms often is hard to characterise, due to the fact that especially wetland plants such as lycopsids are much better preserved and their relative contribution to fossil organic matter therefore might not reflect their true regional abundance (Falcon-Lang, 1999). Additionally fossil plants are better preserved in continental strata than in deltaic strata which is intercalated in a marine sequence (Chaloner and Meyen, 1973).

Although discussions have been controverse, it is commonly accepted, that from the Devonian to the Early Carboniferous floral differentiation has been small and that these periods were dominated by an uniform *Lepidodendropsis* flora (Chaloner and Meyen, 1973; Raymond *et al.*, 1985). Nevertheless this has been questioned by Falcon-Lang (1999) lately. The author recognised the presence of growth rings in fossil woods from northern Britain indicating a tropical savanna like climate for this region. Growth rings are typical for gymnosperms and Falcon-Lang (1999) therefore suggested that at least Northern Britain during the Early Carboniferous was dominated by gymnosperms.

For the Late Carboniferous in contrast to the predating periods at least three flora provinces have often been recognised (Chaloner and Meyen, 1973; Anderson *et al.*, 1999). Most of Gondwana was dominated by the *Glossopteris* flora. The Euramerian flora realm expanded from North America and Europe in the West

to the Balkans in the East and from northern Turkey to the Donetz Basin. It is supposed to have been dominated by arborescent lycopsids for example *Lepidophloios, Sigillaria* and *Bothrodendron*, the sphenopsids, the genera of fern like foliage including pteridosperms and true ferns and the gymnosperm genus *Cordiates* (Chaloner and Meyen, 1973). The Angaran flora occupied the presentday Siberia and Mongolia. It shared many genera of the Euramerian flora realm, but some forms were present only in Angara while many typical Euramerian members were absent (Chaloner and Meyen, 1973). In general the Angaran flora was much poorer in lycopodes while *Cordaites*-like plants and pteridosperms were predominant (Chaloner and Meyen, 1973; Raymond *et al.*, 1985).

1.3 Preservation of Terrestrial Organic Matter

In general terrestrial sedimentary organic matter is derived from plants and bacteria, while animals are only minor contributors. Especially humic coals represent sedimentary organic matter characterised by high proportions of autochthonous organic matter i.e. predominantly plant remains.

Humic coals are distinguished from sapropelic coals due to their organic matter being primary derived from woody tissues of vascular plants. Sapropelic coals in contrast consist of varying amounts of allochthonous organic and inorganic matter. They are subdivided in two groups, cannel and boghead coals. Both lack stratification and show a homogeneous texture (Taylor *et al.*, 1998a). Boghead coals in contrast to cannel coals, are characterised by high amounts of algal remains. In contrast to humic coals, sapropelic coals normally do not go through a peat stage but are formed in oxygen-deficient shallow waters (Taylor *et al.*, 1998a). Humic coals normally are formed by compaction and induration of plant remains which often have been deposited as peat in mires, mainly in swamps and raised bogs (Taylor *et al.*, 1998a; Killops and Killops, 1993). A widespread development of peat did not occur until the emergence of vascular plants (Taylor *et al.*, 1998a).

The formation of coals is supported by different environmental factors. An important factor according the formation of coals is a high primary production. Primary

production is affected by the rate of photosynthesis and therefore light, the availability of water and a moderate temperature (Killops and Killops, 1993). A wet and warm climate supports the formation of a luxuriant flora characterised by a fast growth and a short need of time to renew itself (Taylor *et al.*, 1998a). However a moderate climate does not only increase the rate of plant growth but also the rate of decomposition (Taylor *et al.*, 1998a). The second and even more important factor supporting the formation of coals is the depositional environment. Accumulation of organic matter within an ecosystem results from the incapability of decomposers to cope with the input of organic matter into sediments (Moore, 1989). Besides the rate of burial the amount of oxygen present in sediments is an important factor. Respiratory activity of aerobic microorganisms is predominantly reduced by low concentrations of oxygen (Moore, 1989). Anoxic conditions therefore support the preservation of organic matter and the formation of coals. A stagnant groundwater close to the ground surface depletes the decomposition of organic matter by microorganisms. Both tectonic and paleogeographic factors do additionally influence the formation of coal bearing strata (Courel, 1989a). Sea level variations due to strong subsidence may result in a drowning of the peat while slow subsidence results in the rotting of the peat. Although coal seams accumulate organic matter, the amounts represent only a minor fraction of what has originally been available (Taylor *et al.*, 1998a).

1.3.1 Composition of Coals

Coals are characterised by heterogeneousity of organic matter due to the different plants and plant organs they are composed of (Taylor *et al.*, 1998a). The organic matter of coals is described by three maceral groups: vitrinite, liptinite and inertinite.

Vitrinite is the major maceral group present in humic coals. It is believed to predominantly consist of coalified lignin (Hatcher *et al.*, 1989). Lignins are constituents of xylem an important constituent of the vascular system in higher plants. Lignin consists of aromatic nuclei, aliphatic side chains and hydroxyl groups, phenolic hydroxyl groups and methoxyl groups. It shows a high resistance against

microbial or fungal degradation. Hatcher *et al.* (1989) found a predominance of catechol-like units showing a high degree of aromatic-ring substitution within progressive thermal alteration of xylem originating from gymnosperm wood. Besides lignin, cellulose (polysaccharides) is an important constituent of the xylem. Cellulosic materials however are no important contributors to macroscopical organic matter in coals, due to their significant depletion via early microbial degradation (Taylor *et al.*, 1998a). Nevertheless they participate in the formation of vitrinite (Hatcher *et al.*, 1989). Tannins are also important contributors to the vitrinite group. They consist of high-molecular weight compounds incorporating phenolic structures and, like lignins also are relatively resistant against degradation. *Sphagnum* for example is an important peat former in temperate climatic zones, due to the relatively high contents of tannins (Taylor *et al.*, 1998a).

The liptinite group in contrast to the vitrinite group, shows high amounts of aliphatic constituents. The organic matter originates from plant materials like sporopollenin, cutin, resins, waxes, fats etc. (Taylor *et al.*, 1998a). Fatty compounds are major contributors to this maceral group and can be divided into low molecular soluble and insoluble highly polymerized groups. Nitrogen-containing compounds like amino acids, low molecular weight peptides but also low molecular carbohydrates, such as sugars and starches normally are recycled initially. The majority of low molecular compounds originates from the so-called secondary metabolism of plants. The most important compound classes that due to preservation become concentrated in the sedimentary organic matter are acetogenins, steroids, resins, waxes, cutins, suberins, carotenoids, flavonoids, xanthones, tannins, alkaloids and porphyrins. The biological function of these compound classes varies widely. Additionally some of these compounds are restricted to certain plant groups (Fig. 1.5).

1.3.2 Controls on the Composition of Sedimentary Organic Matter

Besides the early depositional environment and the contributing organisms the composition of coals is strongly influenced by both microbial and thermal degra-

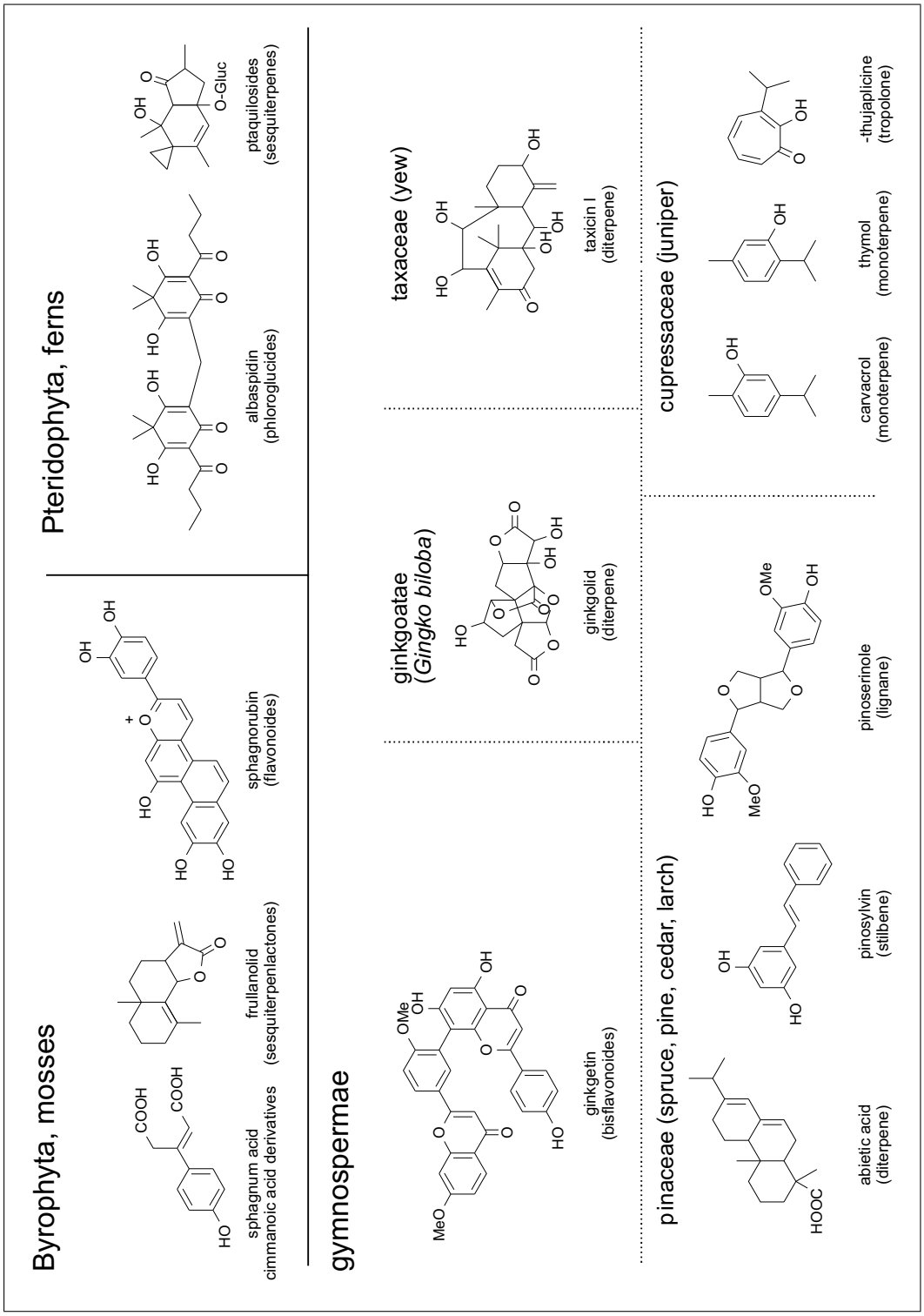

Figure 1.5: Low molecular weight constituents of early land plants with chemotaxonomic significance

dation. These degradations affect the organic matter to different degrees, i.e. some compounds are more resistant while others are degraded easily (Killops and Killops, 1993). The transformation of organic matter in the sediments is subdivided into three different stages: diagenesis, catagenesis and metagenesis.

Sedimentation but also diagenesis are the levels on which organic matter is mainly destroyed by oxidative processes (oxygen, sulphate and further electron-acceptors and early diagenetic fermentation). The transformations taking place during diagenesis occur under mild conditions. The most important factor influencing the magnitude of diagenesis is the activity of microorganisms. The depletion of compounds via microbial degradation is accompanied by the formation of organic material originating from these decomposers. Some compounds are not altered significantly by biological activities but are transformed via isomerisation reactions. Biogenic compounds often possess a configuration, that is thermodynamically instable. Alteration of these configurations under mild conditions results in the formation of equilibrium mixtures. Biopolymers may be destroyed via biotic or abiotic degradation and form liquids, gases and solid residues. The loss of functional groups, especially hydroxyl groups characterises the early processes of coalification (Taylor *et al.*, 1998a). These defunctionalisation reactions result in the rise of carbon contents and in the formation of geopolymers. At the end of diagenesis the majority of carboxy groups is removed, aliphatic structures are significantly depleted and organic matter mainly consists of kerogen (Tissot and Welte, 1984). Aerobic bacteria besides fungi are the most important decomposers of organic matter. They act at the top of the peat and consume the oxygen from the atmosphere. Their activity is best in neutral to weakly alkaline media (Taylor *et al.*, 1998a). To inhibit microbial activity a stagnant oxygen poor groundwater is of advance. Beyond the top of the peat aerobic activity is soon replaced by anaerobic activity, showing a reduced microbial life (Taylor *et al.*, 1998a).

Diagenesis is followed by catagensis. Catagenic processes start at vitrinite reflectances beyond 0.5% R_r (Tissot and Welte, 1984). With increasing burial depth, temperature and pressure are considerably increased (Tissot and Welte, 1984). Whereas the increase of temperature results in chemical reactions, the alteration of physico-structural properties is attributed to pressure (Taylor *et al.*,

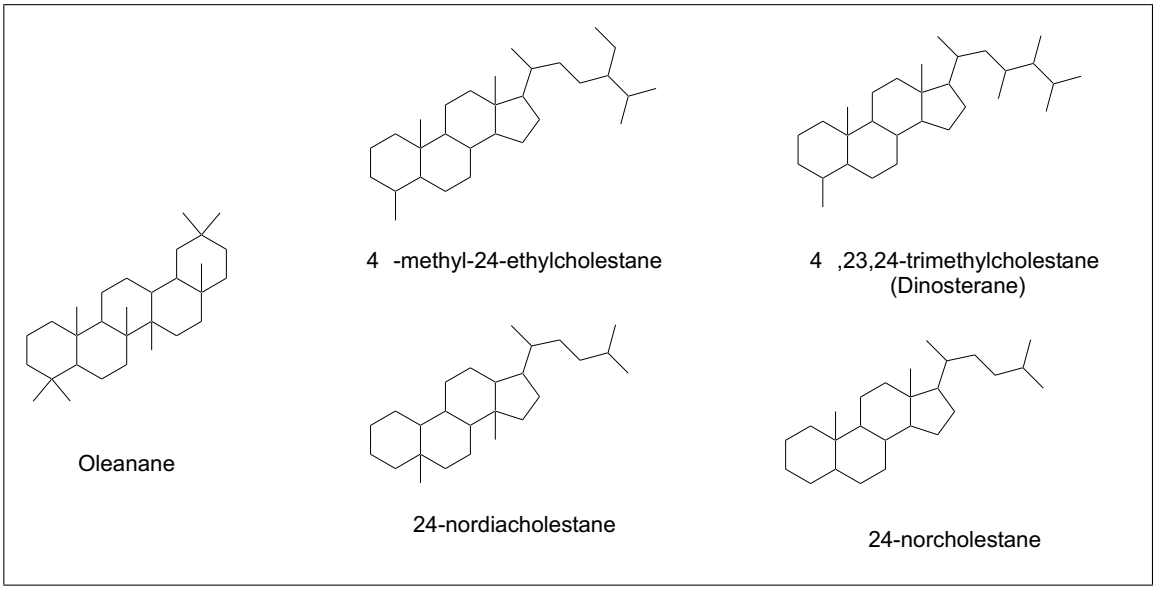

Figure 1.6: Age-specific biomarkers

1998a). Catagenic processes result in the loss of hydrogen via liquid and gaseous hydrocarbons. Loss of hydrogen results in the increase of aromatic structures. At the end of catagenesis aliphatic hydrocarbons have completely disappeared (Tissot and Welte, 1984).

Coals that have not experienced catagenesis show minor alteration in the composition of organic matter. Plant structures often are recognisable. This does not account for more mature coals, where aromatisation and defunctionalisation result in a significant alteration of biogenic structures. Organic matter that has been altered by metagenesis according its degree of aromatisation does not differ significantly despite its origin.

1.4 The Significance of Individual Organic Compounds

1.4.1 Biomarkers: Organic Fossils

The significance of molecular compounds in terrestrial organic matter is variable. Some compounds are constituents of many organisms while others are specific for a particular group of organisms. Some compounds are produced due to transformations via diagenesis and catagenesis while others retain their specific molecular structure within these processes. Biomarkers are organic compounds attributed to known biological precursors which retain their specific structure within the sedimentary record. The value of biomarkers results from the fact, that they are stable at moderate temperatures and may still be present in sediments when recognisable fossils are already absent (Moldowan *et al.*, 1994).

Biomarkers may provide information on origin, redox potential and maturity. Long chain *n*-alkanes and -fatty acids for example are attributed to the cuticular waxes of higher plants and therefore are an indicator for terrestrial organic matter. Hopanes have a bacterial origin and indicate the contribution of microorganisms to the sedimentary record. Pristane and phytane in contrast are the oxidation and reduction products of the side chain from chlorophyll. Although their presence in the sedimentary organic matter is of low significance according the contributing organisms the ratio of pristane/phytane is diagnostic with regard to the redox conditions during early sedimentation. Gammacerane on the other hand is a compound indicating hypersaline depositional environments. Ratios based on the distribution of different isomers for example for hopanes but also alkylphenanthrenes may also serve to estimate the thermal maturity of the organic matter.

1.4.2 Age-Specific Biomarkers

Age-specific biomarkers are organic compounds that can not only be attributed to a certain biological source but that also are specific for a certain geological age. The organic compounds that are age-specific biomarkers have to be significant for a group of organisms that appeared at a certain geological age. Age-specific biomarkers therefore are supposed to maintain important information about the evolution of the Earth´s environment in common and of individual organisms in special. Although long chain *n*-alkanes and -fatty acids, are age-specific biomarkers, as they originate from higher plants which had not evolved until the inhabition of terrestrial environments occurred, they normally are not diagnostic. This results from the fact, that the evolution of land plants occurred during the Middle Paleozoic and that organic matter which is subject to investigations, often postdates this era. Many other compounds that might be characteristic often are not unambiguously produced by a specific groups of organisms. Although vanillin for example is the main product within the oxidation of lignins derived from gymnosperms, it has also been found in bryophytes (Thomas, 1986). Due to this vanillin is not suitable as an age-specific biomarker.

A more exact age-specific biomarker is oleanane (Fig. 1.6). This compound is suggested to derive from β-amyrin, which is a constituent of angiosperms. The presence of angiosperms, and therefore of β-amyrin is restricted to periods of the Cretaceous and younger. Nevertheless findings of oleanane in a coal originating from the Pennsylvanian and investigations on the DNA of modern angiosperms indicate that evolutionary processes resulting in the formation of angiosperms predate the Cretaceous (Martin *et al.*, 1989; Moldowan *et al.*, 1994).

Beside oleanane, few other age-specific biomarkers are known. The occurrence of 4-methylsteroids (Fig. 1.6) in the Paleozoic and Mesozoic ages correlates with the fossil record of acritarchs and dinoflagellates (Moldowan and Talyzina, 1998). The presence of 4-methylsteroids in fossil organic matter therefore normally is taken as an indication that acritarchs and dinoflagellates had already evolved and have been contributors. 24-Norcholestane (Fig. 1.6) on the other hand has been attributed to the presence of diatoms (Holba *et al.*, 1998). Although the biologi-

cal precursor of 24-norcholestane is unknown, the compound shows a significant increase in samples from the Jurassic and Cretaceous. This strongly correlates with the evolution and distribution of diatoms.

Although age-specific biomarkers may contribute significantly to the understanding and knowledge of evolutionary processes, few are known. This is due to the fact that among the bulk of organic compounds known, only few are diagnostic for particular organisms and do additionally preserve the significance of their molecular skeleton at moderate temperatures. The few age-specific correlations of Moldowan *et al.* (1994), Moldowan and Talyzina (1998) and Holba *et al.* (1998) additionally base on aliphatic hydrocarbons (Fig. 1.6). This probably is due to the fact, that especially for aliphatic hydrocarbons biogenic relationships are easily established as modifications of the biogenic skeleton are either weak or still recognisable. Additionally aliphatic hydrocarbons for low molecular weight compounds are the best investigated compound classes in organic geochemistry.

2 Objectives

This thesis was prepared in the framework of a project of the current DFG-program "Evolution of the system Earth during the Late Paleozoic in the mirror of sediment geochemistry". This program aims to investigate paleoenvironmental conditions during the Late Paleozoic in detail which in turn based on the correlations for different projects serve to provide a common time scale of this geological period. The Late Paleozoic is a period when important marine, terrestrial, tectonic and atmospheric changes occurred. However, there is no detailed knowledge of these transformations. Although for example paleoclimate and -tectonics of the Late Paleozoic have been subject to broad investigations (Ross, 1999; Scotese *et al.*, 1999), knowledge on details is limited and correlations of different data are rare. This on one hand is due to the fact, that many factors like for example the composition of the atmosphere and climate can only be established indirectly. Additionally the age-specific correlation of sediments from different locations is difficult. The knowledge about the evolution of both marine and terrestrial systems is limited by this lack of age-specific correlations. Fossils may serve to the knowledge of terrestrial evolution, however they are rare in the Late Paleozoic and do not generally indicate phylogenetic relationships. Investigations on secondary metabolites, i.e. molecular organic matter may serve to overcome this problem. However, besides the fact that it also often can not be attributed to a certain period unambiguously, the organic matter additionally often has been subject to significant alterations based on biotic and abiotic processes. These alterations normally result in the loss of valuable biogenic information.

This thesis bases on investigations of extractable organic matter of Paleozoic coals and clastic sediments containing elevated amounts of terrestrial organic matter. They aim to describe the biochemical evolution of plants in the Paleozoic on the

basis of geochemical characterisations of the low molecular weight compounds. To overcome the problem of biotic transformations coals were preferentially selected. They consist of high proportions of terrestrial organic matter, which normally was not altered significantly by biodegradation. Regarding strong abiotic, i.e. thermal alterations, sample origins normally are from areas that are known to have suffered weak thermal transformations. The detailed qualitative and quantitative characterisation of the extractable organic matter, besides on aliphatic and aromatic hydrocarbons is especially focussed on the nitrogen, sulphur and oxygen (NSO) containing compounds. This focus aims to investigate relationships between aromatic hydrocarbons and their functionalized analogues. Besides the fact that functionalized compounds often are highly abundant in terrestrial organic matter, they in comparison to aromatic and aliphatic hydrocarbons additionally are supposed to contain enhanced information according biogenic relationships. However the possibility exists that the relationships are not only genetic but may also result from abiotic oxidation/reductions or polymerisations in the sedimentary history of the organic matter.
Prior to the estimation of the biogenic significance of individual compounds and compound classes these factors therefore have to be considered. It will be investigated whether relationship between different compounds are due to their kinetic or thermodynamic stability and whether they are formed randomly in sediments. The biogenic value of compounds and compound classes which show weak correlations will then be considered. The potential biogenic precursors of these characteristic compounds and compound classes will then be searched based on the chemotaxonomy of modern land plants. To estimate the age-specific value, both the qualitative and quantitative appearance of these compounds and compound classes will be considered in correlation to the geological age of the organic matter. The predominant evolutionary challenge within the plant kingdom in the Late Paleozoic to the actual knowledge is the evolution of conifers from gymnosperms. Conifers but also gymnosperms in general are characterised by strong phylogenetic differences to other plants of the Late Paleozoic. Therefore especially the occurrence of markers for conifers are investigated in detail.
Aiming to get a complete overview on the organic matter of the investigated samples, a co-project of the University of Aachen, Germany, focussed on the corresponding biogenic particles and macromolecules of the same samples. A corre-

lation of the results of both projects was supposed to support the findings for the single projects.

3 Geographical and Geological Setting of the Samples

A total of 40 Late Paleozoic samples were investigated. Their stratigraphic age extends from the Middle Devonian to the Late Permian. Nine samples were ascribed to the Permian, 23 to the Upper Carboniferous, seven to the Lower Carboniferous and one to the Devonian period. The investigated samples originate from different locations (Fig. 3.1). Although the majority of the samples are coals, some are sediments containing predominantly terrestrial organic matter and two are fossils of vascular plants.

Due to the need of relatively low maturity samples, locations are limited to areas beyond the Variscan front in Eastern, Northern and Central Europe, i.e. especially England and the Moscow Basin. Furthermore the investigations mainly base on coals as they represent well preserved organic matter (OM) deposited in swamp and bog areas. The availability of sample series from one stratigraphy which imply the complete Late Paleozoic is difficult to obtain. Due to the fact, that most of the locations do not imply stratigraphies of the complete Upper Paleozoic, the origin of the samples expands from East Greenland and Spitsbergen in the North, England and Germany in the West, France in the South and Russia but also South China in the East (Fig. 3.1). Although flora may differ for different locations, except for the coal from South China (Late Permian), provided by Y. Sun (Hebei Institute of Architectural Science and Technology, Handan, PR China) and the coal from the Petchora Basin provided by H. Kerp (University of Münster, Germany), all belong to the Euramerian flora realm (Fig. 3.1).

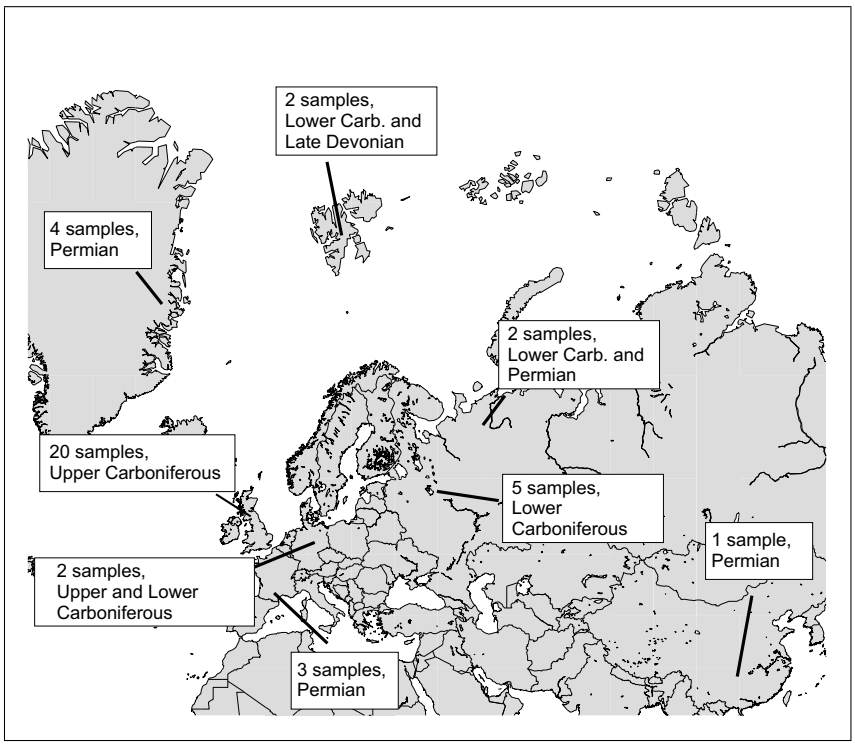

Figure 3.1: Geographic origin of Late Paleozoic samples

Table 3.2 refers to the locations of the samples and their lithology. In the following a brief overview about the origin and the specific conditions of sedimentation for individual basins will be given.

3.1 North England

The Upper Carboniferous samples from North England were provided by the British Geological Survey (England). They were obtained from English sites of the Pennine Basin. The Pennine Basin is located in Central and Northern England and North Wales, and is limited by the Southern Uplands in the North and the Wales-London-Brabant Massif in the South. The investigated samples are from Cumberland, Durham and Northumberland.

At the beginning of the Carboniferous, Northern Britain has drifted northwards into tropical latitudes. The area, after Caledonian tectonism and intrusion, was re-

Table 3.1: Geological age of the investigated samples

Sample	Period	Epoch
E 49710	Permian	Lower Zechstein
E 49748		Ravnefjeld Formation
E 49749		
E 49750		
E 49751		
E 48990		Guadalupian
E 48478		Rotliegend
E 48479		
E 48480		
E 48996	Upper Carboniferous	Westphalian D
E 48388		Westphalian C
E 48389		
E 48390		
E 48214		Westphalian B
E 48216		
E 48430		
E 48403		Westphalian A
E 48220		
E 48392		Westphalian A (?)
E 48393		
E 48394		
E 48395		Namurian (?)
E 48396		
E 48397		
E 48398		
E 48400		Namurian
E 48401		
E 48405		
E 48425		Namurian C
E 48382		unknown
E 48383		
E 48384		
E 48985	Lower Carboniferous	Upper Viséan
E 48986		
E 48987		
E 48988		
E 48989		
E 48993		
E 48991		
E 48992	Devonian	Givetium-Frasnium

Table 3.2: Geographical origin, lithology and rank of the samples

Sample	Origin	Location	Lithology and rank
E 49710	South China	Dahe Mine	high vol. bit. coal
E 49748	East Greenland	Jameson Land	slate
E 49749	East Greenland	Gauss Halvo	silt
E 49750	East Greenland	Jameson Land	silt-slate
E 49751	East Greenland	Kap Stosch	silt, laminated slate
E 48990	Russia	Petchora Basin	medium vol. bit. coal
E 48478	South France	Lodève Basin	
E 48479	South France	Lodève Basin	
E 48480	South France	Lodève Basin	
E 48996	Germany	Lugau-Oelsnitz	high vol. bit. coal
E 48388	England	Keekle	high vol. bit. coal
E 48389	England	Keekle	high vol. bit. coal
E 48390	England	Keekle	high vol. bit. coal
E 48214	England	Potato Pot	high vol. bit. coal
E 48216	England	Potato Pot	high vol. bit. coal
E 48403	England	Rowlands Gill	mud-/ siltstone
E 48220	England	Potato Pot	high vol. bit. coal
E 48392	England	Distington I	high vol. bit. coal
E 48393	England	Distington I	high vol. bit. coal
E 48394	England	Distington I	high vol. bit. coal
E 48395	England	Distington I	high vol. bit. coal
E 48396	England	Distington I	high vol. bit. coal
E 48397	England	Distington I	high vol. bit. coal
E 48398	England	Distington I	high vol. bit. coal
E 48400	England	Dearham	high vol. bit. coal
E 48401	England	Dearham	high vol. bit. coal
E 48405	England	Rowlands Gill	high vol. bit. coal
E 48382	England	Throckley	sandstone
E 48383	England	Throckley	high vol. bit. coal
E 48384	England	Throckley	mudstone
E 48985	Russia	Moscow Basin	cannel-boghead coal
E 48986	Russia	Moscow Basin	cannel-boghead coal
E 48987	Russia	Moscow Basin	soft brown coal
E 48988	Russia	Moscow Basin	soft brown coal
E 48989	Russia	Moscow Basin	soft brown coal
E 48993	Germany	Borna-Hainichen	high vol. bituminous coal
E 48991	Spitsbergen	Pyramiden	high vol. bit. coal
E 48992	Spitsbergen	Mimerdalen	cannel-coal
E 48430	fossil	*Sigillaria*	Westphalian B
E 48425	fossil	*Mesocalamites cf. Taitianus*	Namurian C

duced to a peneplain due to erosion and a relatively stable block area was formed. Sedimentation in the Carboniferous was influenced by tectonic, climatic and eustatic forces. In the Dinantian, limestones, shales, sandstones and coals were deposited during repeated cycles of marine transgressions and regressions. In the Namurian to mid-Westphalian the basin experienced influx of terrestrial sediments from the north-west and north-east and a freshwater deltaic environment with lagoons and coal swamps developed. Thin marine bands proof periodic marine incursions. In the Westphalian environmental conditions became more continental. The Pennine basin subsided during most of the Westphalian and deposition occurred persistently close to sea level (Guion and Fielding, 1986). The Variscan orogeny resulted in an regional uplift during latest Carboniferous times. For the Pennine Basin these effects are less evident than for the continent of Europe.

3.1.1 West Cumberland- the West Cumbrian Coalfield

The West Cumbrian Coalfield of West Cumberland is of Westphalian age. It is located in the north western part of the Pennine Basin. It has a size of 233 km^2 and extends from Maryport southwards to Whitehaven, bordering the coast at a length of 26 km and a width of 7 km (Fig. 3.2). Additionally it extends eastwards from Maryport for an area of 19 km length and 2.5 km width. The West Cumbrian Coalfield is bordered by the Solway Syncline from the Canonbie Coalfield in the North. The coal-bearing strata of the West Cumbrian Coalfield has a thickness of 400 m. Samples were obtained from four locations in West Cumberland. While the boreholes from Distington and Dearham represent the Namurian, the opencasts Keekle and Potato Pot represent the Westphalian (Fig. 3.2).

Namurian - Hensingham Group

Depositional environments in the Early Carboniferous were almost exclusively marine. The Namurian represents the transition from these predominantly marine conditions to almost exclusively freshwater deltaic environments in the Westphalian (Young and Armstrong, 1989). The majority of the sediments were sup-

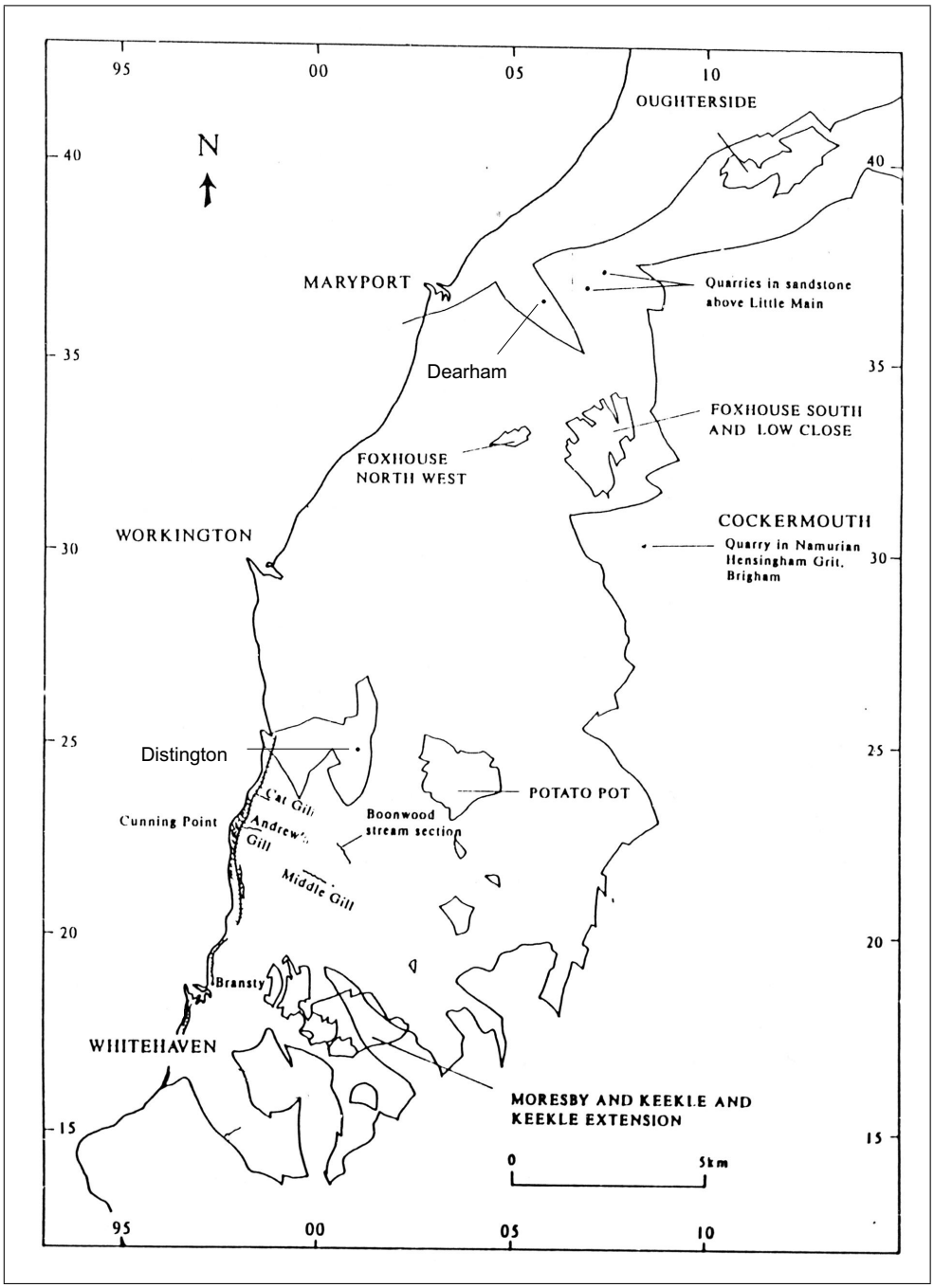

Figure 3.2: Location of the boreholes and opencast sites from the Cumberland district investigated in this thesis; after Jones (1992)

Table 3.3: Samples of the Hensingham Group

Sample	Origin	Depth [m]	Epoch
E 48392	Distington I	12.26	Westphal A(?)
E 48393	Distington I	12.66	Westphal A(?)
E 48394	Distington I	12.86	Westphal A(?)
E 48395	Distington I	35.65	Namurian
E 48396	Distington I	56.60	Namurian
E 48397	Distington I	72.00	Namurian
E 48398	Distington I	110.55	Namurian
E 48400	Dearham	44.75	Namurian
E 48401	Dearham	55.32	Namurian

plied from the Northern part of the Pennine delta (Hallsworth *et al.*, 2000). The Hensingham Group (Fig. 3.3) experienced little attraction, due to its little economic importance (Young and Armstrong, 1989; Young and Boland, 1992). It is located between the First Limestone (Chief Limestone Group), representing the beginning of the Namurian and the *Gastrioceras subcrenatum* marine band at the base of the coal measures of the Westphalian (Young and Boland, 1992). Sediments of the Hensingham Group consist of mudstones, laminated siltstones and sandstones with thin coal seams (Young and Boland, 1992). The Group crops out in the northern part of the West Cumbrian district but also as inliers at Distington (Young and Boland, 1992). The Hensingham Group thickens from 50 m in the north to 110 m and 140 m in the east for the Distington and Rowhall Farm (Dearham) boreholes. The lower part of the Hensingham Group, the Hensingham Grit (Fig. 3.3) is a prominent sandstone layer which is suggested to have been deposited near-coast (Young and Armstrong, 1989). The two boreholes at Distington I and Rowhall Farm (Dearham) represent sediments of the Hensingham Group that have been subject to recent investigations. While the sediments of Distington extent to the Westphalian A, younger strata than Namurian is absent for the Rowhall Farm Borehole (Dearham) (Fig. 3.3). Therefore it may be presumable that the three uppermost samples of Distington, that have been investigated belong to the Westphalian A (Table 3.3, Fig. 3.3). The coals of Distington possess a thickness of few centimeters and overlie mudstones or siltstone seatearths. Two samples from Distington (Table 3.3, depth: 35.65 m and 110.55 m) contain

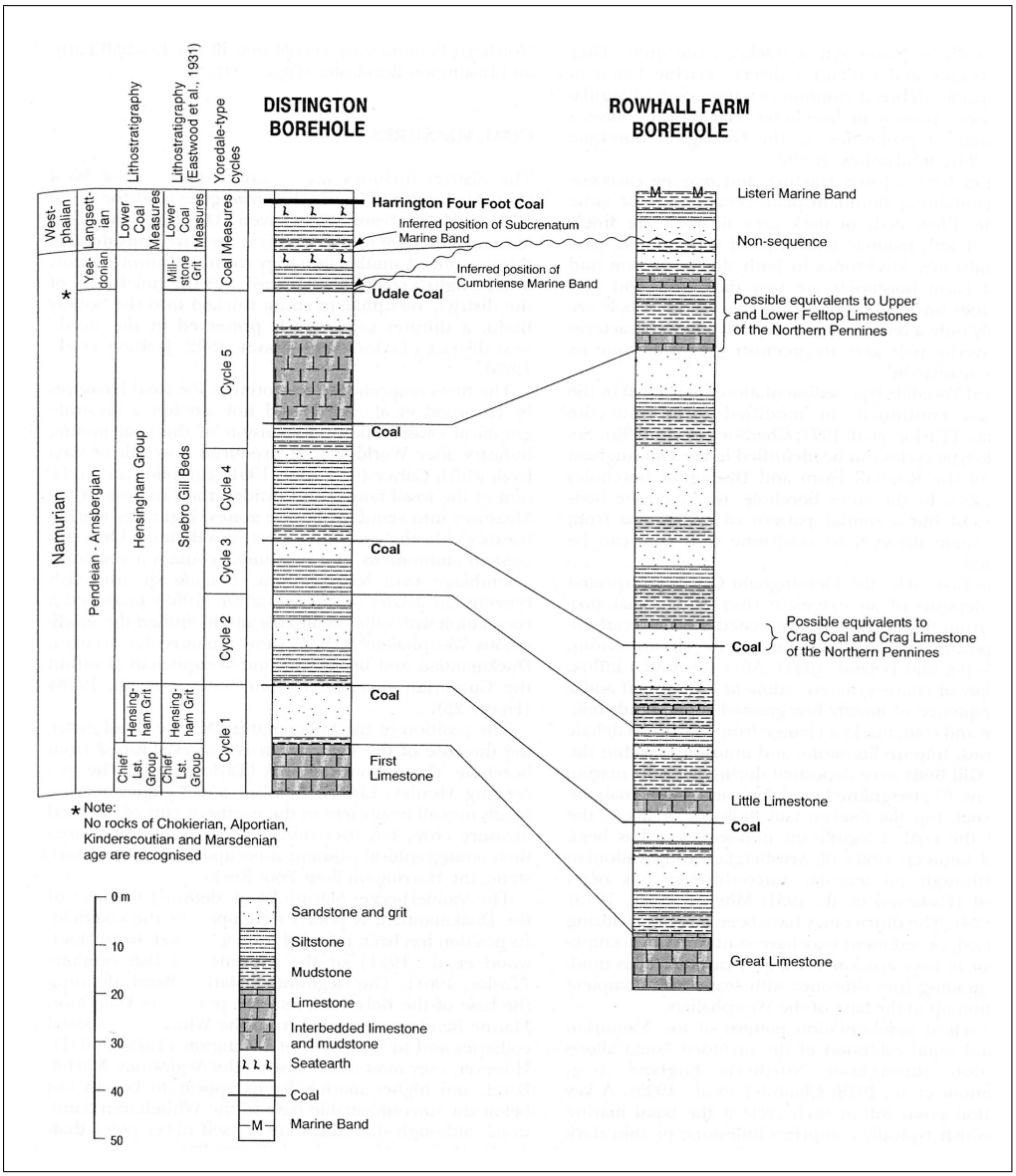

Figure 3.3: Stratigraphy of the Hensingham Group in the Distington Borehole and correlation with the Rowhall Farm Borehole; after Young and Boland (1992)

Table 3.4: Samples of the Westphalian

Sample	Origin	Depth [m]	Period	Seam
E 48388	Keekle 2194	32.0	Westphalian C	-
E 48389	Keekle 2194	40.0	Westphalian C	-
E 48390	Keekle 2194	64.0	Westphalian C	-
E 48214	Potato Pot	24.7	Westphalian B	Rattler
E 48216	Potato Pot	29.9	Westphalian B	Yard
E 48220	Potato Pot	77.8	Westphalian A	Sixquarters

enhanced amounts of total sulphur. Therefore it is presumable that they were deposited under marine influence.

Westphalian

The West Cumbrian Coalfield is of Westphalian age, with coal seams of the Westphalian A and B being predominant. The Westphalian strata was deposited on an upper delta plain to lower alluvial plain, extending from present day north Europe to north America. In Britain shallow lakes were infilled by sediment supplied from a systems of fluvially-dominated lacustrine deltas, transported by a system of channels (Young and Boland, 1992; Jones, 1992). Deposition on these delta plains, took place in interdistributary bays and lakes. Extensive peat-forming mire complexes developed. Rare glacio-eustatic sea level rises periodically led to marine conditions. A gradual northward thickening of the Westphalian is related to increased regional subsidence towards the Solway Basin. The coal measures are thinner than those in most other English coalfields. The Westphalian of the West Cumbrian Coalfield is limited by the *Gastrioceras subcrenatum* marine Band and the reddened strata of the Pre-Permian, which has been subject to intensive oxidation (Young and Boland, 1992). Eight marine bands are recognised for the Westphalian indicating marine intrusions (Fig. 3.4). While coals often form only minor components of the succession, sandstones, mudstones and siltstones are strongly abundant (Fig. 3.4). For the Westphalian A and B, coal seams are named and well correlated for different boreholes; in contrast coal seams of the Westphalian C lack names (Fig. 3.4).

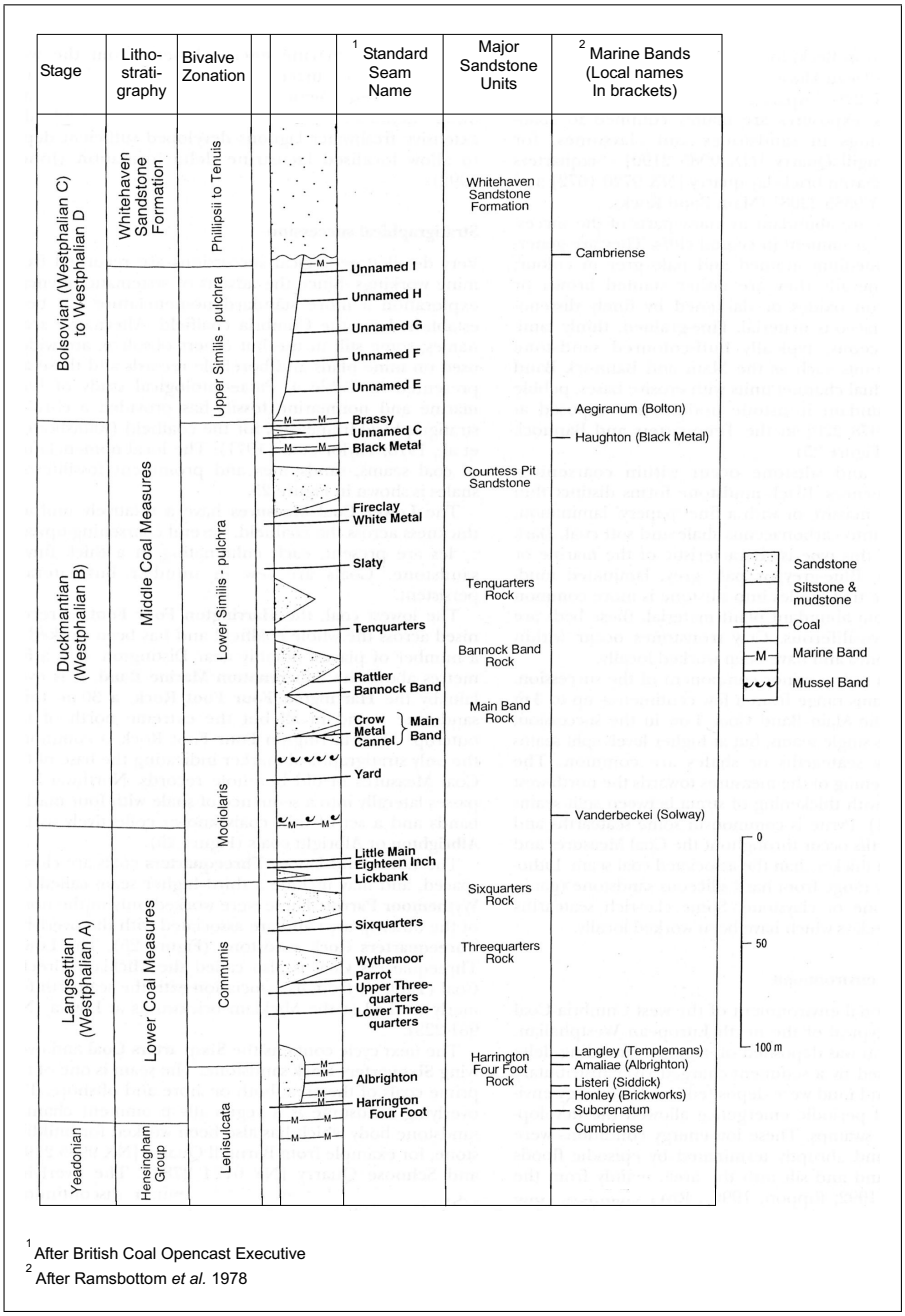

Figure 3.4: Generalised vertical stratigraphy in the Cumberland district; after Young and Boland (1992)

Both locations, Potato Pot and Keekle represent outcasts located in the Southern Part of the West Cumbrian Coalfield. The three coal seams from Potato Pot belong to the Westphalian A and B respectively (Fig. 3.4, Table 3.4). One coal is ascribed to the Sixquarters seam, one of the prime coal seams of the area, which is overlain by the Sixquarters sandstone. The two Westphalian B coal seams from Potato Pot (Table 3.4, Yard and Rattler) are located between mussel beds. The three coals from Keekle are ascribed to the Westphalian C.

3.1.2 Durham and Northumberland

Two samples originate from Rowlands Gill, located in the district of Tyne and Wear in Durham, while three were obtained from the Throckley borehole, Northumberland. The areas are also part of the Pennine Basin and therefore probably have been subject to depositional conditions strongly corresponding to the ones of Cumberland. Additionally it has been suggested, that these areas in particular in comparison to the rest of the Pennine Basin have been slightly elevated. Therefore marine bands are significantly less abundant and thin in relation to the rest of the Pennine Basin (Jones, 1992).

The two samples from Rowlands Gill originate from the Westphalian A and the Namurian (Table 3.5). The upper Westphalian A strata, where one of the samples is from corresponds to the Lower Coal Measures of the West Cumberland Coalfield (Fig. 3.3), while the lowest Westphalian A and Namurian strata comprise what is often termed the Millstone Grit and Upper Limestone Group (Mills, 1982). The Namurian sample from Rowlands Gill originates from the Millstone Grit. In the area of Durham and the eastern parts of Northumberland only Westphalian B and the middle and upper part of Westphalian A strata crop out (Mills, 1982). The Westphalian strata of the area consists of rhythmic alternations of sandstone, siltstone, mudstone, shale, coal seatearth and uncommon shales, while coal comprises a very small proportion of the total thickness (Mills, 1982).

The three samples from the opencast mine of Throckley in Northumberland could not be assigned with certainty (Table 3.6). The district, due to its complex,

Table 3.5: Samples from Rowlands Gill

Sample	Origin	Depth [m]	Period
E 48403	Rowlands Gill	51.61	Westphalian A
E 48405	Rowlands Gill	93.80	Namurian

Table 3.6: Samples from Throckley

Sample	Origin	Depth [ft]	Period
E 48382	Throckley	396.11	
E 48383	Throckley	559.10	
E 48384	Throckley	848.30	

laterally variable succession, its poor exposion and numerous faults has received little attention from geologists (Holliday and Pattison, 1987). Solid rocks of this area are mainly of Namurian and early Westphalian age and broadly comprise the Upper Limestone Group and the Millstone Grit (Holliday and Pattison, 1987). Carboniferous sediments of Northumberland comprise a laterally and vertically variable repetitive sequence dominantly of sandstones, siltsones and mudstones. This is suggested to result from alternating marine and fluvio/deltaic conditions, like described for the other parts of northern England previously (Holliday and Pattison, 1987). The Throckley borehole has been examined in 1964-1965 aiming to establish a sequence from undoubted Lower Coal Measures down to the Great Limestone (Holliday and Pattison, 1987). It therefore is assumed, that the three samples of the Throckley borehole are of Namurian age. One is a mudstone (848.30 ft), one a coal (559.10 ft) and the third a mudstone (396.11 ft).

3.2 Moscow Basin

Five samples, provided by H. Kerp originate from the Moscow Syneclise and were deposited during the Viséan (Table. 3.1). The Moscow Basin is located on the East European platform, one of the largest Precambrian Cratons of the world. The craton is covered by extensive Devonian and Carboniferous sediments which ex-

perienced only insignificant intraplate tectonic movements (Alekseev *et al.*, 1996). The Moscow Basin is located in the center of this craton and expands from North to South about 600 km and more than 1000 km from East to West (Fig. 3.5). It is limited by the Voronezh Anticline southwards and the Tokmovo Uplift and the Ok-Tsna Swell eastwards (Alekseev *et al.*, 1996; Nikishin *et al.*, 1996). Changes in sea-level are attributed to tectonical movements of the uplift areas, resulting in regional changes of facies. The Moscow Syneclise due to its geology can be subdivided into a western, southern, northern and eastern part. After the East European platform has been uplifted during the Lower Devonian, shallow-marine carbonate sequences were deposited during the Devonian and Carboniferous. The sequences include several subordinate terrigenous intervals. A significant regression in the latest Famenian was followed by a short transgression in the early Tournaisian, covering almost the entire area with marine waters (Alekseev *et al.*, 1996). During the Upper Tournaisian to Middle Viséan a regression occurred. The eastern part of the Basin was uplifted and eroded, while the southern and western parts were flooded and organic rich sediments were deposited. The Upper Viséan is characterised by a strong transgression followed by a regression at the boundary between the Lower and Middle Carboniferous (Alekseev *et al.*, 1996). Eight coalfields, predominantly located in the southern part of the Moscow Basin are known. Most of the coals are assigned to the Bobrikian and Tulian (Middle Viséan) period, and seldomly to the Radaevkian (Lower Viséan).

The five coals from the Moscow Basin (Table 3.2), with one exception can not be assigned to a certain age. One coal belongs to the Tulian Group of the Middle Viséan. Within the formations of this group, clays and limestones of a marine fauna are predominant, with sand, silt but also coals being present. Due to the coal-bearing sediments being present at these times the investigated samples may originate from the Middle, perhaps also the Lower Viséan, when organic-rich sediments were deposited primarily in the southern part of the basin (Alekseev *et al.*, 1996). All coals of the Moscow Basin can be classified as loose, laminated dull brown coals, characterised by vitrinite reflectance values in the range of 0.35-0.45% R_r (Bode and Feist, 1928). Coals of the Moscow Basin show the presence of mio- and macrospores and cuticules. These cuticules often consist of the steams and branches of *Lycophytes*, the predominating flora of this area. Besides the dull

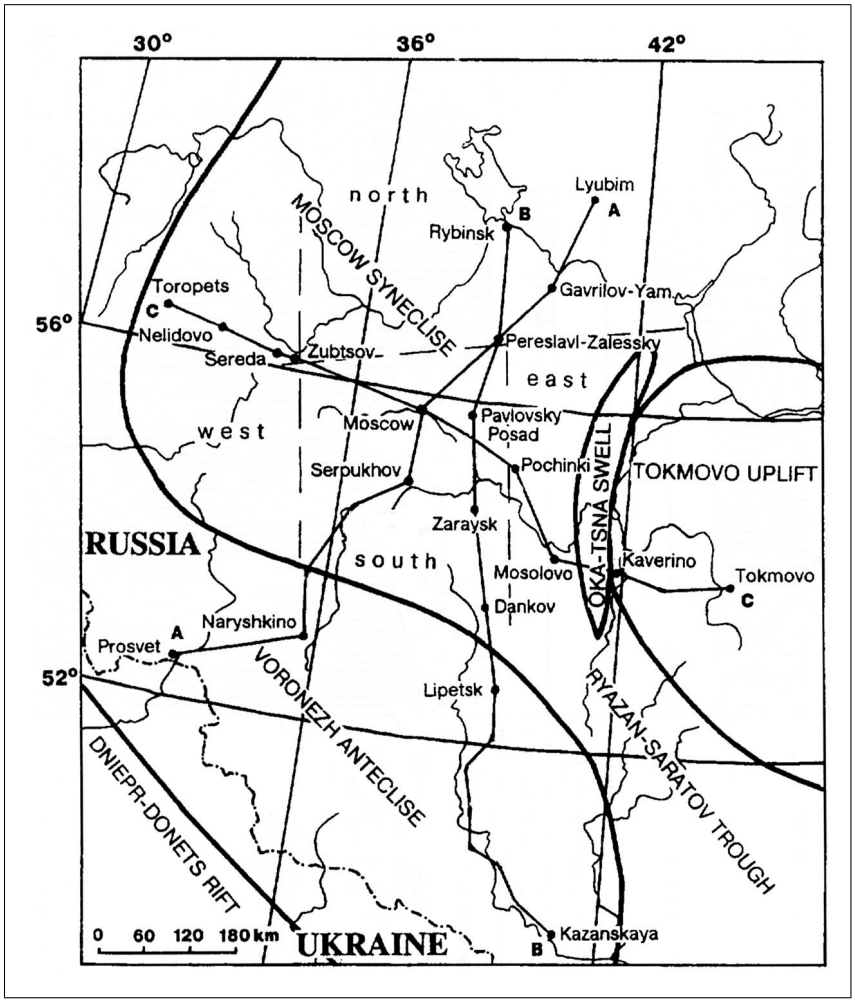

Figure 3.5: Regional setting of the Moscow Syncline. Main tectonic elements are marked by solid lines, while dashed lines display the western, southern, eastern and northern part of the basin. The map is modified after Alekseev *et al.* (1996)

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brown coals, cannel coals have also been reported to be present, while boghead-coals occur seldomly (Bode and Feist, 1928; Bode, 1930). The depositional environments were presumed to be strongly anoxic (Jacob, 1961; Taylor *et al.*, 1998b) while climate was predominantly tropical (pers. com. W. Peters-Kottig, University of Münster, Germany).

3.3 East Germany

Two coals from East Germany, one ascribed to the Westphalian D and one to the Viséan were provided by H. Kerp. Both originate from the Erzgebirge, Saxony. The coal from the Westphalian D originates from Lugau-Oelsnitz and was taken from the Deutschlandschacht at a depth of 2.00 m beneath the ground. The coal from the Viséan originates from a surface seam. During the Carboniferous Saxony was placed in subvariscian foredeeps. The Lower Carboniferous is characterised by marine dominated depositional environments whereas the Upper Carboniferous is predominantly paralic. The vegetation for both periods has been tropical (pers. com. W. Peters-Kottig).

3.4 East Greenland-Ravnefjeld Formation

Four sediments of the East Greenland Basin (Jameson Land, Kap Stosch and Gauss Halvø) (Fig. 3.6) were provided by J. A. Bojesen-Koefoed (Geological Survey of Denmark and Greenland, Denmark). They belong to the Ravnefjeld Formation, deposited during the Late Permian, the Capitanian equivalent to the Zechstein 1 (Christiansen *et al.*, 1993).

Upper Permian and Mesozoic sediments outcrop extensively in this part of the East Greenland Basin (Fig. 3.6). The basin extends from North to South about 400 km and 80 km from East to West. On the western side the Caledonian mountain belt forms the boundary, whereas the Norwegian Sea is the East boundary. The East Greenland Basin was formed by a series of westward-tilted fault blocks (Birkelund and Perch-Nielsen, 1976). During the Upper Permian a transgression from north-east occurred, accompanied by minor regressions. Afterwards the East Greenland Basin subsided (Piasecki and Stemmerik, 1991). The Upper Permian sediments have a thickness of 15-20 m and are thickest in the southern part of the basin, i.e. Jameson Land because of regional subsidence due to thermal concentration (Christiansen *et al.*, 1992). The sediments are thinner along the margins of the basin (Christiansen *et al.*, 1993). They predominantly consist of marine shales and

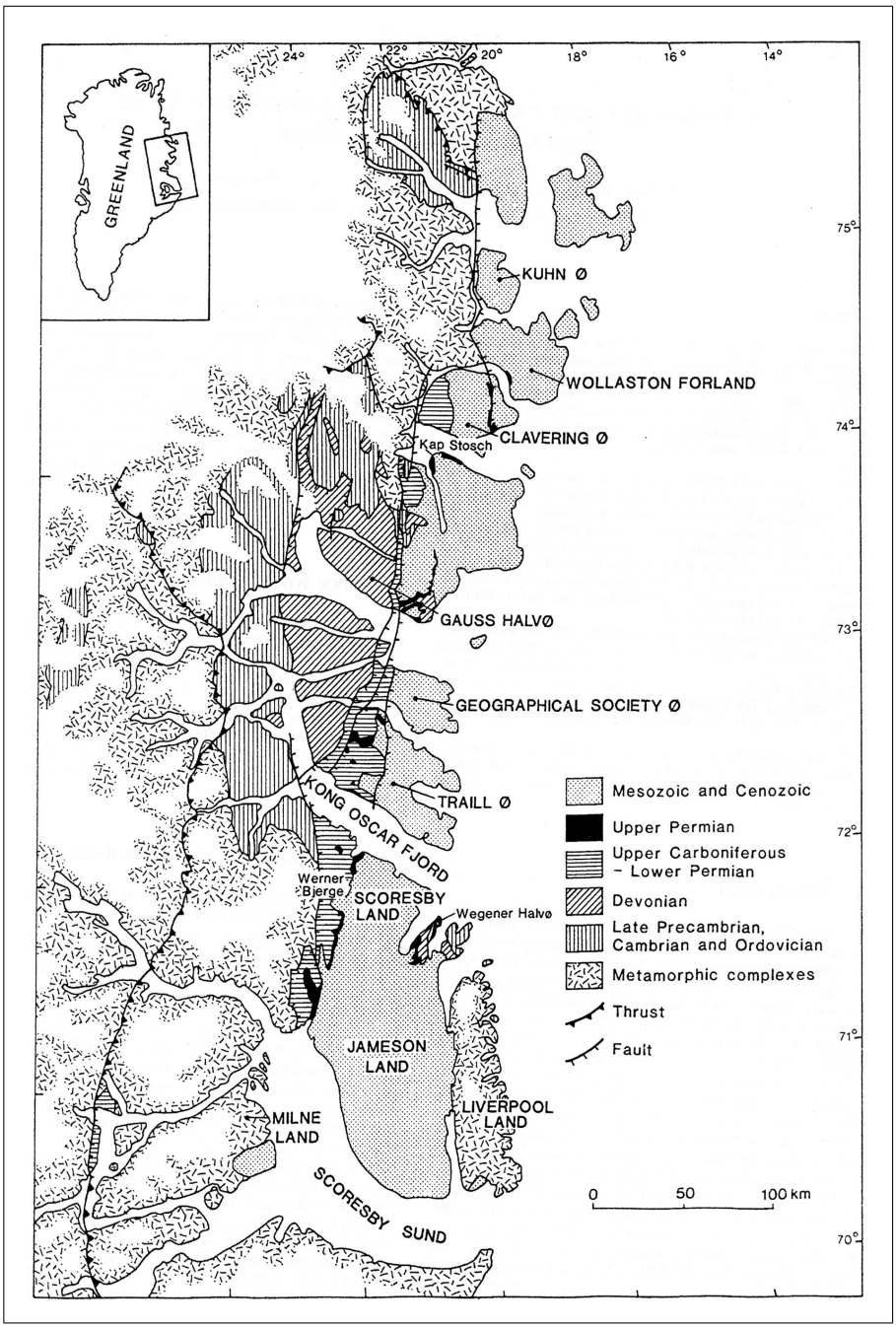

Figure 3.6: Geological map of East Greenland after; Christiansen *et al.* (1992)

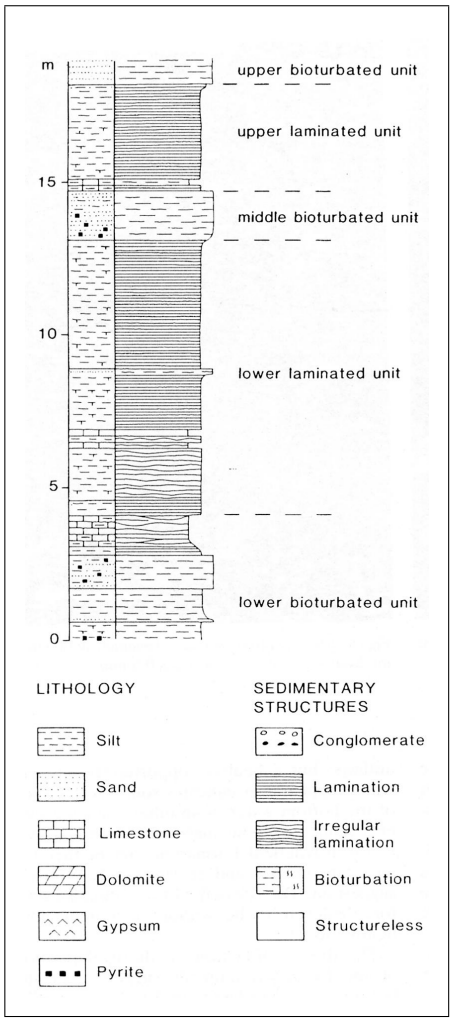

Figure 3.7: Stratigraphy of the Ravnefjeld Formation; investigated by Piasecki and Stemmerik (1991)

carbonates. The depositional environment was controlled by climatically driven, major eustatic sea-level changes (Christiansen *et al.*, 1992, 1993). The formation consists of five subunits (Fig. 3.7). Two intervals are organic-rich, laminated clay-silt layers, deposited under anoxic conditions at high eustatic sea-levels. These intervals are separated by three intervals of gray bioturbated siltstones, deposited under more oxic conditions and during low stands of sea-level (Christiansen *et al.*, 1993; Piasecki and Stemmerik, 1991). The formation is overlain by grey bioturbated shales due to increased siliciclastic supply and a relative fall of sea level in the latest Permian (Piasecki and Stemmerik, 1991). In the Upper Permian climatic conditions in East Greenland have been hot and arid (Christiansen *et al.*, 1992). However it was suggested, that the relative lowering in sea level was associated with a short-term change in climate from arid to humid correlating to the bioturbated intervals (Christiansen *et al.*, 1993). Although the depositional environment of the sediments from the Ravnefjeld Formation is primarily marine, the investigated samples contain notable amounts of terrigenous material (pers. com. J. A. Bojeson-Koefoed). Therefore the samples are suggested to originate from the bioturbated intervals, containing coalified type III kerogen (Piasecki and Stemmerik, 1991). Although sulphate reducing bacteria did not strongly affect the bioturbated intervals, sulphate contents are generally high for the Ravnefjeld Formation (Piasecki and Stemmerik, 1991). Outcrop samples from the Ravnefjeld Formation, except for the Werner Bjerge-Scoresby Land area and the Wegener Halvø are immature (Christiansen *et al.*, 1992).

3.5 Lodève Basin

Three sediment samples originate from the Lodève Basin (Fig. 3.8), southern France and were provided by F. Körner and J. Schneider (University of Freiberg, Germany). The basin is located in the southern part of the French Central Massif and extends 26 km from East to West and 10 km from North to South. It is bordered by the Montagne Noire in the North and the Tertiary plain of Languedoc in the South. The sediments (Usclas et St. Privat Formation and Formation de Tuilieres-Lorias) were deposited during the Lower Permian (Autunian) in a fluvial

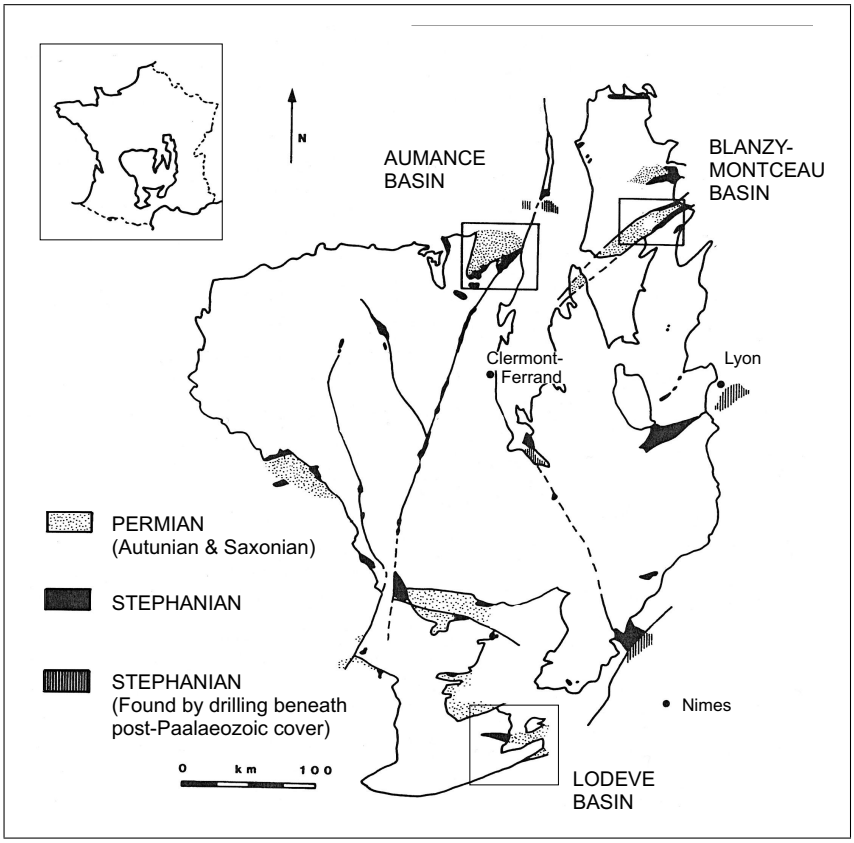

Figure 3.8: Position of the Lodève Basin in Southern France after Courel (1989b)

to lacustrine environment. They discordantly overlay Pecambrian and Cambrian slates, gneisses, granits and dolomites. The climate during sedimentation was humid tropical. The organic matter of the samples is suggested to be a mixture of algae and land plants.

3.6 Spitsbergen

Two coals, provided by H. Kerp (University of Münster, Germany) originate from Spitsbergen. Spitsbergen is the largest island of a group called Svalbard. These island group is located in the northwestern corner of the Barents Shelf (Birkenmajer, 1981). Svalbard has experienced strong vertical and horizontal movements due to the Caledonian Orogeny and has been subject to notable deformations from

the Pecambrian to the Upper Paleozoic. The Caledonian Foldbelt, outcropping in the western and north-central parts of Spitsbergen strongly correlates to the Caledonian belt of East Greenland. After the Caledonian Orogeny during Frasnian and Famenian Svalbard was subjected to intensive compressional events leading to the separation of the eastern plate of Svalbard from the western Greenland plate (Birkenmajer, 1981). The rocks of the Caledonian Foldbelt are formed of Precambrian and Middle Ordovician sediments (Birkenmajer, 1981). At the beginning of the Carboniferous the Svalbard area became part of the continental Barents-Kara platform and was subjected to recurrent denudation and accumulation of mainly terrigenous deposits. The region was tectonically stable from Carboniferous to Late Cretaceous times (Manby and Lyberis, 1996). During the Lower Carboniferous postorogenic molasse basins developed. From Carboniferous to Permian Svalbard is characterised by unstable land-shallow sea conditions. The Carboniferous and Permian of Svalbard can be separated in three regions, characterised by strong differences in lithology.

One of the two investigated coals is a cannel coal which is ascribed to the Upper Givetium or Lower Frasnium. It originates from the Mimerdalen Formation/Dickson Land. The second coal originates from the Mumien Formation, Dickson Land (per. comm. W. Peters-Kottig) and is a cannel coal. Both coals have been deposited in tropical environments (pers. com. W. Peters-Kottig).

3.7 Fossils

The two fossils, provided by C. Hartkopf-Fröder (Geologischer Dienst NRW, Krefeld, Germany) are a *Mesocalamites cf. Taitianus* from the Namurian C and a *Sigillaria* from Westphalian B. Both plants belong to the group of pteridophytes and have been predominant in Upper Paleozoic forests. Although pteridopyhtes inhabited all climatic zones, they diversified strongest and grew highest in tropical regions (Strasburger *et al.*, 1991). While *Sigillaria* belongs to the genus of *Lycopodiopsida*, *Calamites* is ascribed to the *Equisetopsida*. Already in the Devonian these plants reached the size of trees.

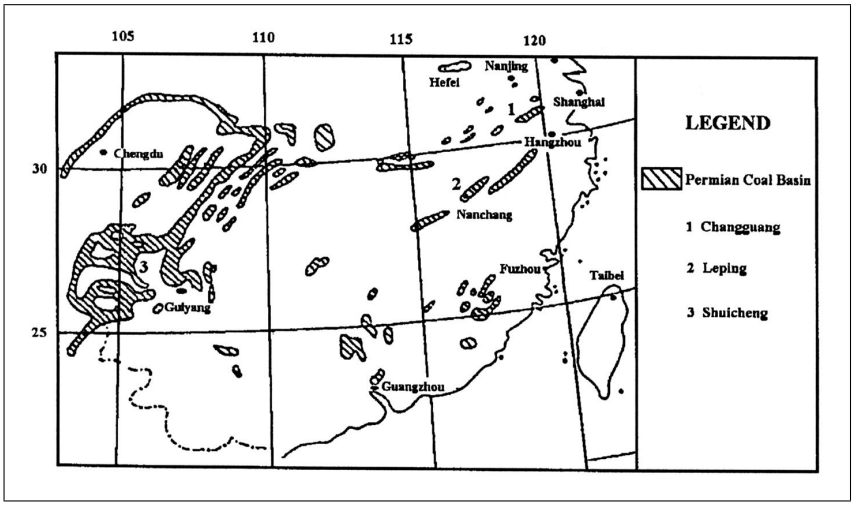

Figure 3.9: Shuicheng Basin and Coal Bearing strata of Southern China; after (Zhong and Smyth, 1997)

For the *Sigillaria* this was due to a secondary growth in thickness and the formation of a supplying system. *Sigillaria* may have reached heights of 40 m and breadth of 5 m. *Sigillaria* inhabited humic areas, due to faint formation of roots expanding near to top of the soils. The plants are characterised by simple leaves up to 1 m length and 10 cm breadth, growing at the end of a little forked stem. At the lower parts of the treetop sporophyllcones were attached to the stem by short branches.

Equisetopsida (*Calamites*), i.e. horsetails are characterised by small leaves in comparison to their stems. Both, leaves and stems are arranged in whorls, this especially for the stems is contrary to the rest of the pteridophytes. In contrast to recent horsetails, Upper Paleozoic *Equisetopsida* were characterised by a great variety in species.

3.8 South China

One of the two samples, not belonging to the Euramerian flora realm is a coal from the Dahe Mine, Shuicheng Basin, Guizhou Province, in Southwest China (Fig. 3.9). The Shuicheng Basin is located in the southern part of the Kangdian

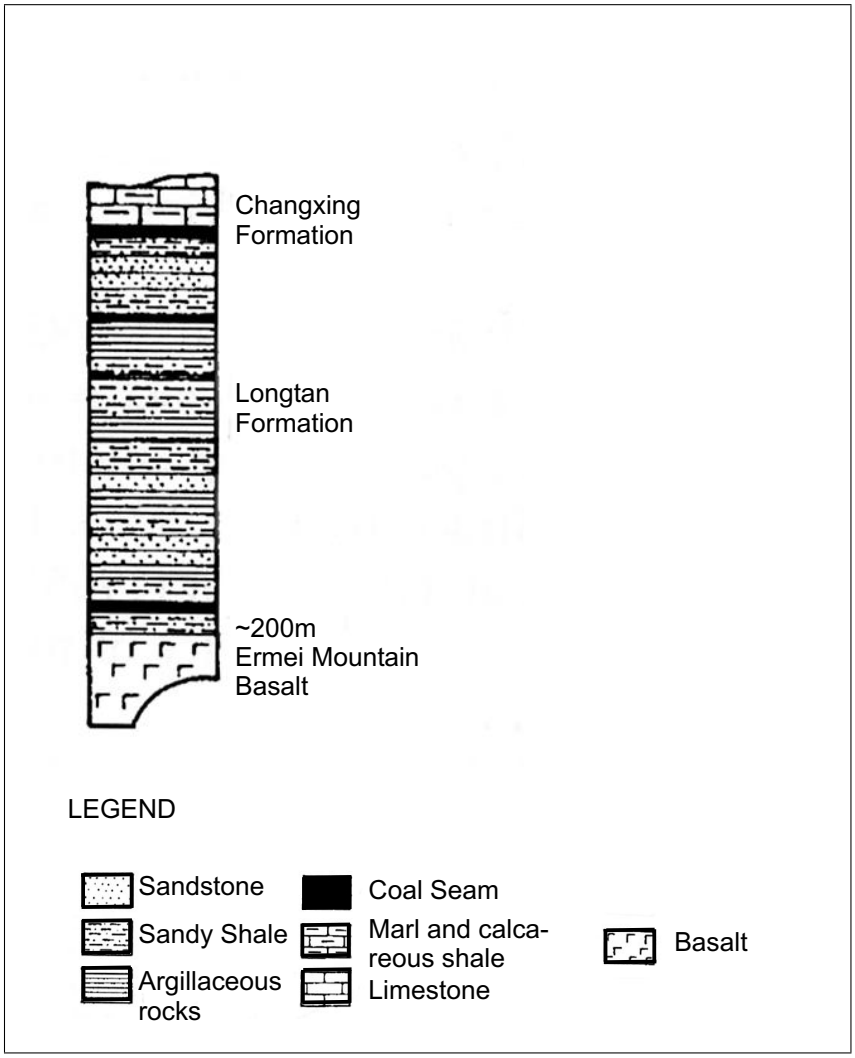

Figure 3.10: Generalised Late Permian stratigraphy in the Shuicheng Basin; after Zhong and Smyth (1997)

Craton and was formed adjacent to a mountainous region on Permian volcanics (Zhong and Smyth, 1997). The coal was deposited during the Lower Zechstein (pers. com. Y. Sun) in a paralic, deltaic depositional system with marine influence on the peat (Zhong and Smyth, 1997). The Late Permian coal-bearing strata of the Shuicheng basin has a thickness of 250 m (Fig. 3.10) (Zhong and Smyth, 1997). The flora in this region was dominated by *Lepidodendron* and the tree fern *Psaronius*. In correspondence to the differences in flora realm, the Chinese coal contains "barkinite", a liptinite maceral widespread in Chinese coals (Zhong and Smyth, 1997; Sun and Wang, 2000).

3.9 Petchora Basin

The second coal not belonging to the Euramerian flora realm comes from the Petchora Basin in Russia and was deposited during the Rotliegendes, Permian. It was provided by H. Kerp (University of Münster, Germany).

The Petchora Basin is ascribed to the Siberian region, where from the beginning of the Upper Permian a separate flora evolved. This Angara or Kusnezk flora realm in contrast to the Euramerian flora realm was dominated by *Cordiates*-like plants and pteridosperms, while lycopydes where minor contributors (Chaloner and Meyen, 1973). During the Rotliegendes, this region experienced cool to temperate climates (pers. com. W. Peters-Kottig).

4 Materials and Methods

All samples were analysed using the same procedure given in Fig. 4.1. Microscopy was not part of this thesis. Prior to further analytical procedures, the samples were crushed to fine powder using a rotating disk mill (0.5 min). Known amounts of an internal aliphatic standard (α-androstane) and an internal aromatic standard mixture (1-phenylhexane, 1-phenylheptane, 1,8-dimethylnaphthalene, 1-phenylnapthalene, ethylpyrene and butylpyrene) were added to the powder of the coals, prior to extraction. The amounts of added standard depended on the TOC contents of these samples.

4.1 Elemental Analysis

Contents of total carbon (TC), total organic carbon (TOC) and total sulphur (TS) were determined using a Leco Carbon-Analyser IR-112. Determination of the contents were carried out in duplicate by total burning of the powdered sample at 1100°C in an induction furnace under an oxygen stream. CO_2 and SO_3 were quantitatively determined by an infrared detector. All measurements were calibrated using certified reference samples. For determination of total organic carbon, carbonates were removed from the samples by treatment with hydrochloric acid prior to measurement.

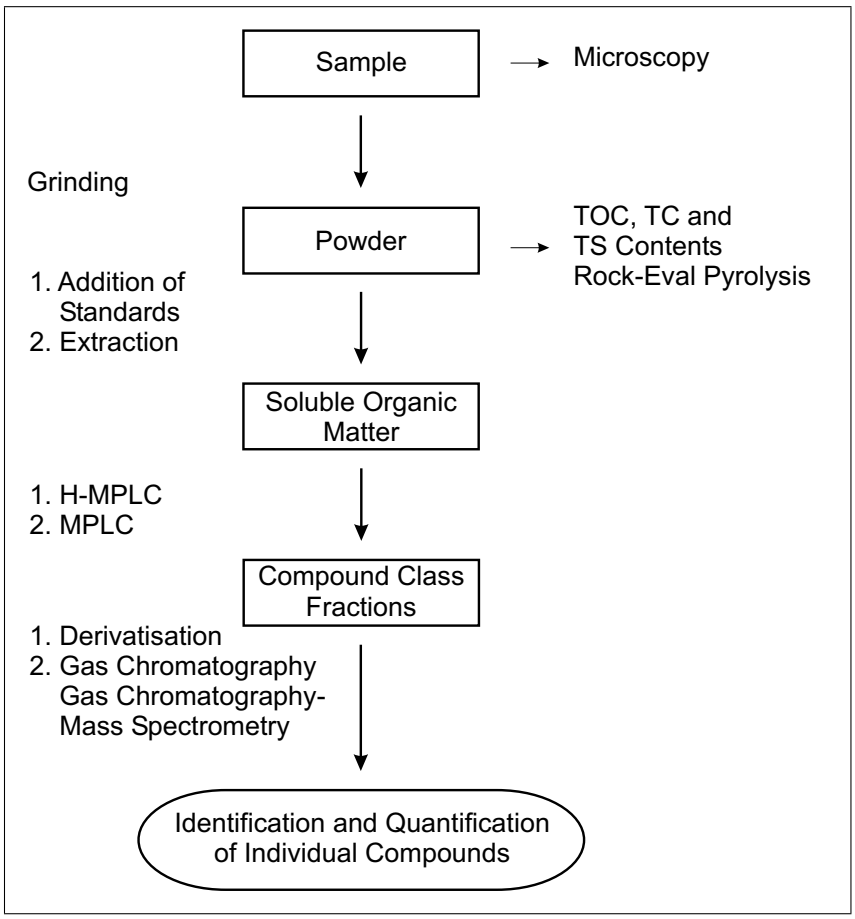

Figure 4.1: Procedures applied in this work

4.2 Rock-Eval Pyrolysis

Rock-Eval measurements were carried out using a Rock-Eval II instrument. The applied procedure refers to the method established by Espitalié *et al.* (1977). An external standard was used for calibration. Peak S1 represents the free volatile organic compounds released in an inert atmosphere (Helium stream) up to a temperature of 300°C. In the following step the temperature is raised from 300°C to 550°C at a rate of 25°C/min. The volatile organic compounds released at this heating period due to cracking of the kerogen are expressed in the peak S2. The CO_2 released between 300°C and 550°C results in the peak S3. The oxygen and hydrogen content of the kerogen is proportional to carbon dioxide (S3) and hydrocarbons (S2) released during Rock-Eval pyrolysis (Peters, 1986). The parameters

S1, S2 and S3 are expressed in mg HC and CO_2/g sample. S2 and S3 provide information about the quality of the organic matter in the sample. By determining the Hydrogen Index (HI) and the Oxygen Index (OI) as the values of S2 and S3 normalized to TOC (mg HC)/(g TOC) and in ($mgCO_2$)/(g TOC) an analogue to the van Krevelen diagram can be constructed. T_{max} is the temperature at which S2 maximises. A plot of HI against T_{max} serves to type the organic matter of the sample and provides information on its maturity.

4.3 Extraction

Amounts of 1-20 g (according to the content of total organic carbon) of homogenized samples were extracted with an azeotropic mixture of chloroform (47 wt%), acetone (30 wt%) and methanol (23 wt%) in two successive 5 min steps, using a modified flow blending method (Radke *et al.*, 1978). After sedimentation of the extraction slurry the supernatant liquid was decanted over a Soxhlet (glass fibre thimbles), concentrated in a Zymmark (Hopkinton, MA, USA) Turbovap 500 evaporator and transferred into 10 ml vials.

4.4 Iatroscan

Iatroscan has been applied to determine the amounts of saturates, aromatics, resins and asphalthenes of the samples from England. Separation of the four fractions is achieved by thin layer chromatography. The amounts of the individual fractions are determined by flame ionization detection (FID). The sample extracts are applied on precleaned Chromarods. The components on the Chromarods are then eluted successively with *n*-heptane, toluene/*n*-heptane (80/20) and dichloromethane/methanol (95/5).

4.5 Liquid Chromatographic Separation into Compound Class Fractions

For the separation of extracts into compound class fractions a liquid chromatographic method developed by Willsch *et al.* (1997) was applied. This method is based on combined polarity/affinity chromatography of the soluble organic matter. Two liquid chromatographic procedures, the Hetero-Medium-Pressure Liquid Chromatography (H-MPLC) and the Medium-Pressure Liquid Chromatography (MPLC) are combined. The extracts are subjected to this column chromatography to recover seven fractions (Fig. 4.2). The high-, medium-, and low-polarity compounds including the aromatic and saturated hydrocarbons are separated according to their polarity. Acids and bases are retained according to their affinity to modified basic and acidic silica. For subdivision of the low-polarity compounds into saturates, aromatics, and low-polarity nitrogen, sulphur and oxygen (NSO) containing compounds conventional MPLC was applied. The solvent of the obtained fractions was removed and the concentrates have been transferred into vials.

4.6 Gas Chromatography

For quantification of *n*-alkanes, pristane and phytane the total aliphatic fractions were analysed by capillary gas chromatography. A Hewlett Pacard 5890 Series II, equipped with an Gerstel on-column-injector, an electronic pressure control (EPC), a fused silica capillary column (HP Ultra I) of 50 m length, 0.2 mm inner diameter and 0.33 μm film thickness and a standard flame ionization detector (FID) was applied. Hydrogen was used as carrier gas at a flow rate of 1ml/min (pressure controlled). The oven temperature was programmed from 90°C (hold time 5 min) to 310°C at a rate of 4°C/min. A Multichrom 2-online data system (Fisons) was employed to store and process retention times and peak areas.

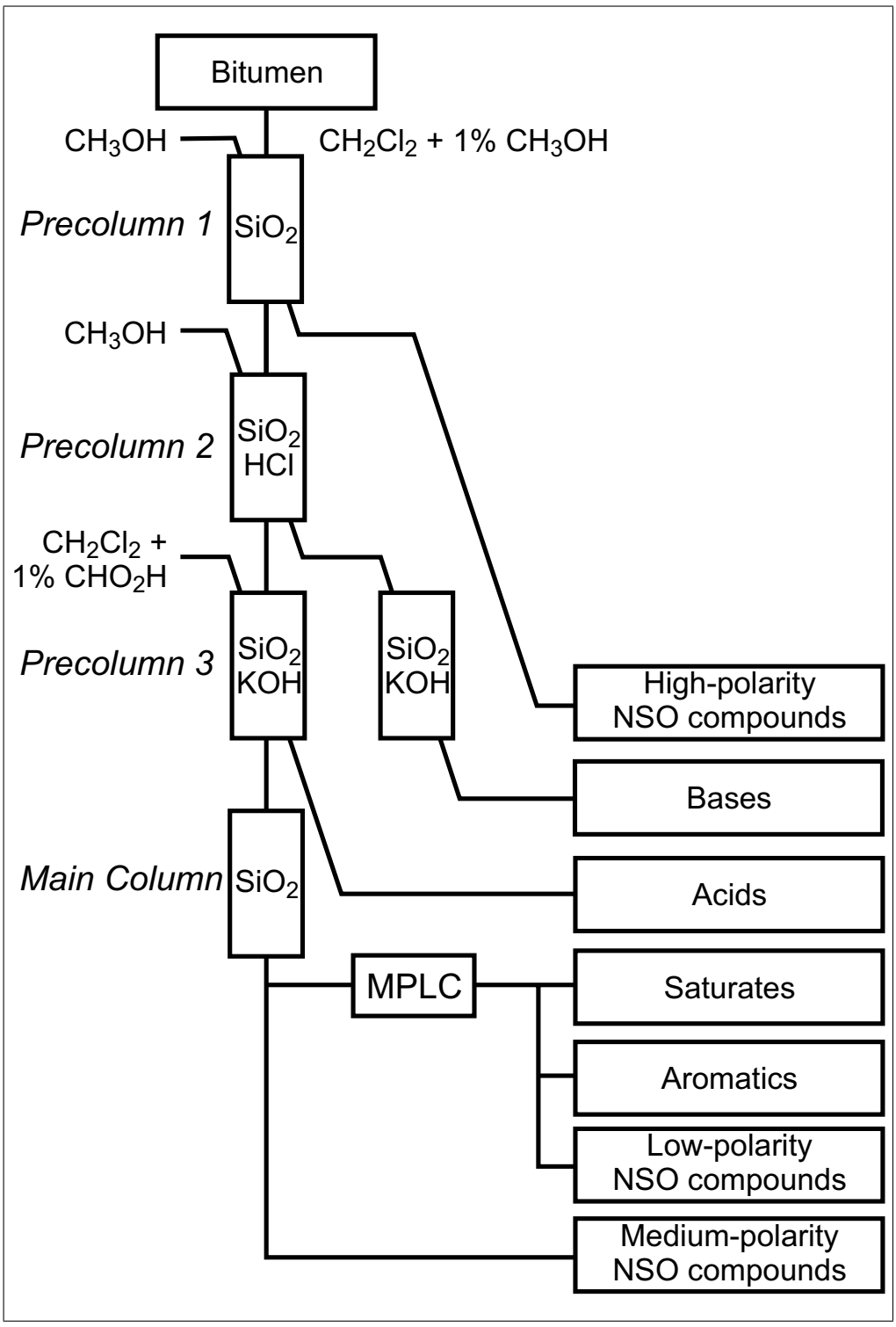

Figure 4.2: Schematic sketch of the liquid chromatographic separation procedure after Willsch *et al.* (1997)

4.7 Gas Chromatography-Mass Spectrometry

Hopanes, steranes and compounds of the other fractions were analysed by gas-chromatography-mass spectrometry (GC-MS) using a Hewlett Packard 5890B gas chromatograph coupled to a Finnigan MAT 95 SQ mass spectrometer. The gas chromatograph was equipped with a temperature-programmable injection system (KAS 3, Gerstel) and a BPX 5 (0.25μ film thickness) fused silica capillary column (SGE) of 50m length and 0.22 mm i.d.. Helium was used as carrier gas with electronic pressure control (EPC 1 ml/min). The oven temperature was programmed from 60 to 340°C (final hold time 8 min) at 3°C/min for the aromatic fraction and from 120 to 340°C for other fractions. Except for analyses of steranes, the mass spectrometer was operated in the EI mode at an electron energy of 70eV and a source temperature of 260°C. Full scan mass spectra were recorded over the mass range of 50-600 Da at a scan rate of 1 sec/decade an inter scan time of 0.2 sec and a scan cycle time of 0.5 sec. Identification of individual compounds was based on gas chromatographic and mass spectral data and partly on comparison with authentic standards.

4.8 Standard Compounds

The internal standards (purity) were obtained from commercial sources; α-androstane, 1-phenylhexane (97%) and 1-phenylheptane (98%) from Riedel-de-Haën, Seelze, Germany; 1,8-dimethylnaphthalene (96%) from E.Merck, 1-phenylnaphthalene (96%) from Aldrich, Steinheim, Germany and 1-ethylpyrene (95%) and 1-butylpyrene (95%) from Varessa, Baden, Switzerland. For identification of compounds the following standards (purity) were purchased from Aldrich, Steinheim, Germany: (1*R*)-endo-(+)-fenchylalcohol (96%), (1*R*)-(+)-camphor (98%), (1*R*,2*S*,5*R*)-(-)-menthol (97%), (1*S*)-(-)-verbenone (99%), isoborneol (95%), [(1*S*)-endo]-(-)-borneol (98%), carvacrol (98%), thymol (99%), 2-biphenylcarboxylic acid (95%), 4-biphenylcarboxylic acid (95%), dimethyl-2,6-naphthalenedicarboxylate (98%), 2,3-naphthalenedicarboxylic acid (95%), 1,4-naphthalenedicarboxylic acid (94%), 9-anthracenecarboxylic acid (99%), 9-

anthracenecarboxylic acid (99%), 4-phenanthrenecarboxylic acid (purity unknown) and 9-phenanthrenecarboxylic acid (purity unknown). 1,2,8-Trimethylphenanthrene, benzo[*b*]naphtho[*1,2-d*]-, benzo[*b*]naphtho[*2,1-d*]- and benzo[*b*]naphtho[*2,3-d*]furan were purchased from Chiron AS, Trondheim, Norway.

5 Bulk Geochemical Results

5.1 Elemental Analysis

For the investigated samples the content of organic carbon (Table A.1) varies widely ranging from 0.2 to 81.5% total organic carbon (TOC). Organic carbon content is generally low for the Permian sediments from Eastern Greenland and Southern France and three samples originating from the Upper Carboniferous. In other samples TOC values exceed 50%. According to Taylor *et al.* (1998a) only few samples can be classified as coals, whereas most represent impure coals. Sulphur contents range between 0.1-9.7% total sulphur (TS), and average at 1-2%. TS is elevated for the Permian samples from East Greenland and South France. Additionally four Upper Carboniferous coals, the Namurian and Westphalian A ones from Rowlands Gill and two Namurian from Distington are characterised by elevated contents of TS. Carbonate contents normally are low but are distinctly higher in the samples from East Greenland and South France and the Namurian from Rowlands Gill (Table A.1).

5.2 Microscopy

Microscopy is not part of this investigations and was carried out by Birgit Gieren (RWTH Aachen, Germany, unpubl. results), according to the methods described by Taylor *et al.* (1998a). Only general trends are therefore presented here.

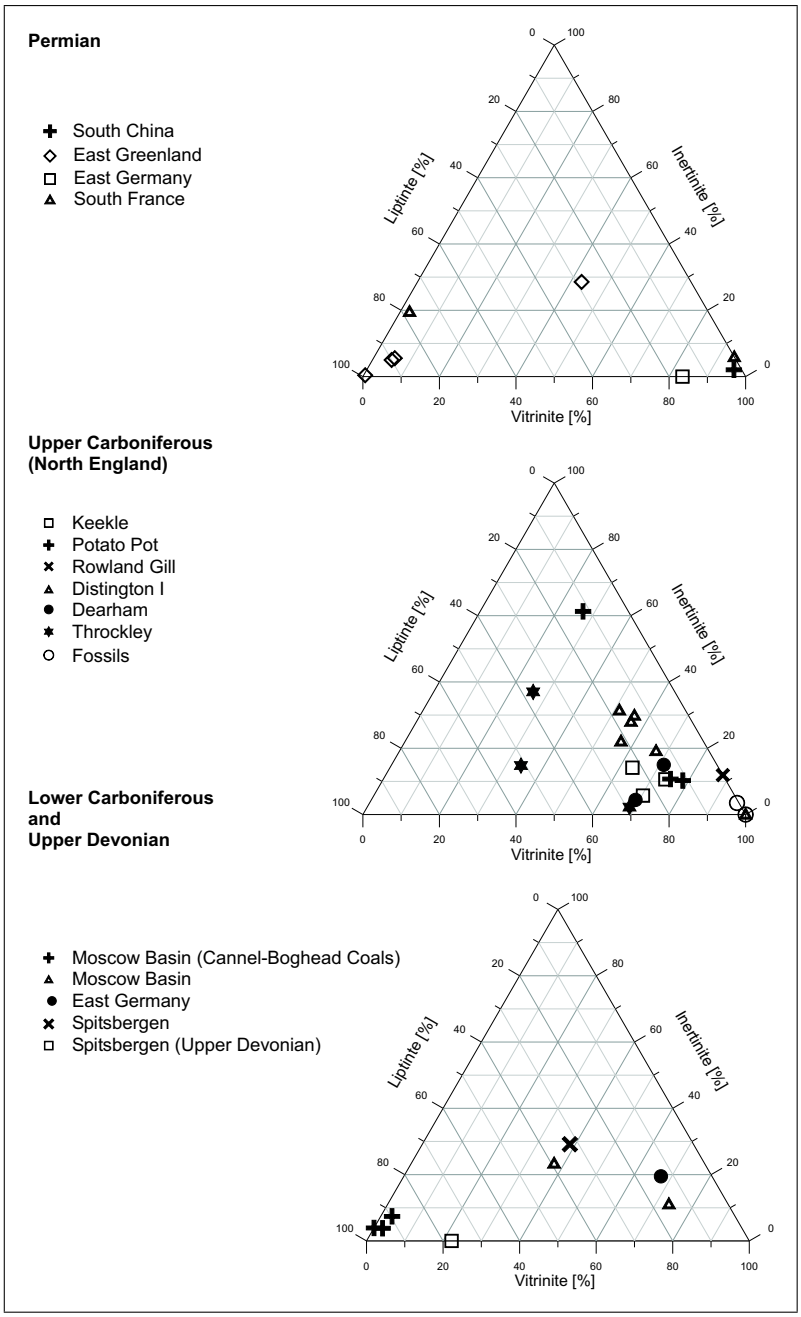

Figure 5.1: Maceral group distribution of Permian, Upper Carboniferous, Lower Carboniferous and Upper Devonian samples

Table 5.1: vitrinite reflectances

Sample	% R_r	Sample	% R_r	Sample	% R_r
E 49748	1.00	E 48216	0.81	E 48425	1.80
E 49749	0.85	E 48430	0.94	E 48382	0.94
E 49750	1.10	E 48403	1.23	E 48383	0.88
E 49751	0.84	E 48220	0.82	E 48384	0.91
E 49710	0.65	E 48392	n.d.	E 48985	0.42
E 48990	1.08	E 48393	0.76	E 48986	0.39
E 48478	n.d.	E 48394	0.81	E 48987	0.32
E 48479	0.59	E 48395	0.78	E 48988	0.41
E 48480	0.75	E 48396	0.68	E 48989	0.37
E 48996	0.57	E 48397	0.72	E 48993	0.57
E 48388	0.83	E 48398	0.67	E 48991	0.88
E 48389	0.88	E 48400	0.78	E 48992	0.76
E 48390	0.84	E 48401	0.77		
E 48214	0.80	E 48405	1.26		

n.d.: not determined

The vitrinite reflectance of the samples ranges from 0.32 to 1.8% R_r (Table 5.1). Vitrinite reflectances (R_r) for the Viséan coals of the Moscow Basin are low and only slightly higher for the German coals from both the Westphalian C and the Viséan (Table 5.1). Further samples show vitrinite reflectances corresponding to the oil window (Table 5.1). The highest maturity is observed for the *Mesocalamites cf. Taitianus* from the Namurian C (Table 5.1).

The four sediments from East Greenland contain high proportions of minerals (Table A.1). In three sediments liptinite is the most abundant maceral group. The forth shows a higher proportion of vitrinites (Fig. 5.1 A). The two coals from Russia and South China contain negligible amounts of minerals but high proportions of vitrinites (Fig. 5.1 A). Among the three French sediments only two were microscopically investigated. They in correspondence to the Permian samples from East Greenland exhibit high proportions of minerals. One of them contains high amounts of vitrinites while the other is characterised by higher proportions of liptinites (Fig. 5.1 A).

The Upper Carboniferous samples are coals or coaly shales. Only few exhibit elevated proportions of minerals. For the majority of the samples vitrinite is the most abundant maceral group (Fig. 5.1 B). One coal (Table A.1) is characterised by high proportions of inertinites and two samples of the Throckley site exhibit no preference of a specific maceral group (Fig. 5.1 B).

Maceral group distribution of the Lower Carboniferous and Devonian samples are also variable (Fig. 5.1 C). Three samples from the Moscow Basin are cannel-boghead coals. They show high proportions of liptinite macerals (Fig. 5.1 C). One sample from the Moscow Basin and the German coal exhibit high proportions of vitrinites. The fifth coal from the Moscow Basin and the Viséan coal from Spitsbergen show no significant preference of either maceral group (Fig. 5.1 C). The Devonian sample from Spitsbergen is a cannel coal, characterised by high proportions of liptinites (Fig. 5.1 C).

5.3 Rock-Eval Pyrolysis

According to the van Krevelen diagram kerogen can be separated into three types. Kerogen containing high proportions of aliphatic moieties is called type I. It exhibits high H/C and low O/C ratios. The material of this kerogen type is primarily rich in lipids, whereas polyaromatic and heteroatomic compounds are rare. Oxygen, present in this type of kerogen normally is ester bound (Tissot and Welte, 1984). Contributors to the organic material of type I kerogen are algae and microbially reworked biomass. The predominant maceral group of type I kerogen is liptinite. Type I kerogen normally is rare. The depositional environments are mainly lacustrine (Killops and Killops, 1993).

Type III kerogen is characterised by relative low H/C but high O/C ratios. Polyaromatic and heteroatomic compounds are highly abundant. Oxygen is preferentially present in ketones and carboxylic acids. The organic matter of type III kerogen is primarily derived from terrigenous sources. Vitrinite macerals, formed from vascular plants are predominant (Tissot and Welte, 1984).

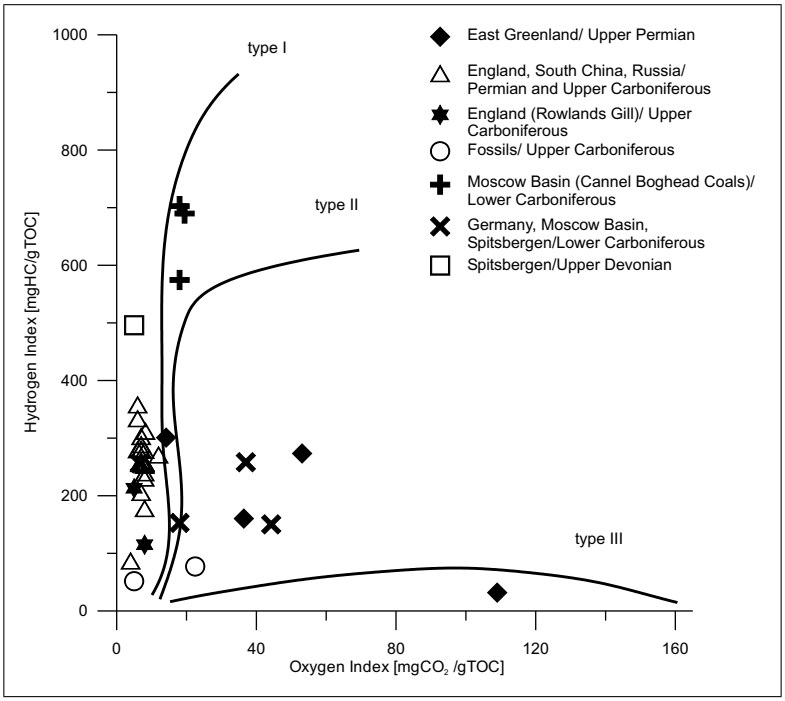

Figure 5.2: HI *vs.* OI (OI values often are low. Kerogen typing in the plot is in clear contrast to the microscopical data and the typing according to the plots of HI *vs.* T_{max} and S2 *vs.* TOC (Fig. 5.3 and 5.4))

Type II kerogen is an intermediate between type I and III and is characterised by relatively high H/C and low O/C ratios. Polyaromatic compounds and heteroatomic groups are more abundant than in type I but less abundant than in type III kerogen. Type II kerogen often originates from marine sediments and autochthonous organic matter, derived from a mixture of phytoplankton, zooplankton and microorganisms, deposited in reducing environments (Tissot and Welte, 1984). It can also be formed from allochthonous material where the macerals from lipid-rich higher plant debris together with plant membrane secretions become concentrated (Killops and Killops, 1993).

The temperature T_{max} at which the maximum amount of volatile organic compounds is released by thermal degradation, is influenced by the maturity of the kerogen. It normally increases with increasing maturity of the organic matter and can be used for quick estimation of the maturity degree (Espistalié, 1985). T_{max} depends on the type of organic matter. The value is strongly related to maturity for oxygen-rich type III organic matter, but is only slightly sensitive to maturity for hydrogen-rich type I kerogen.

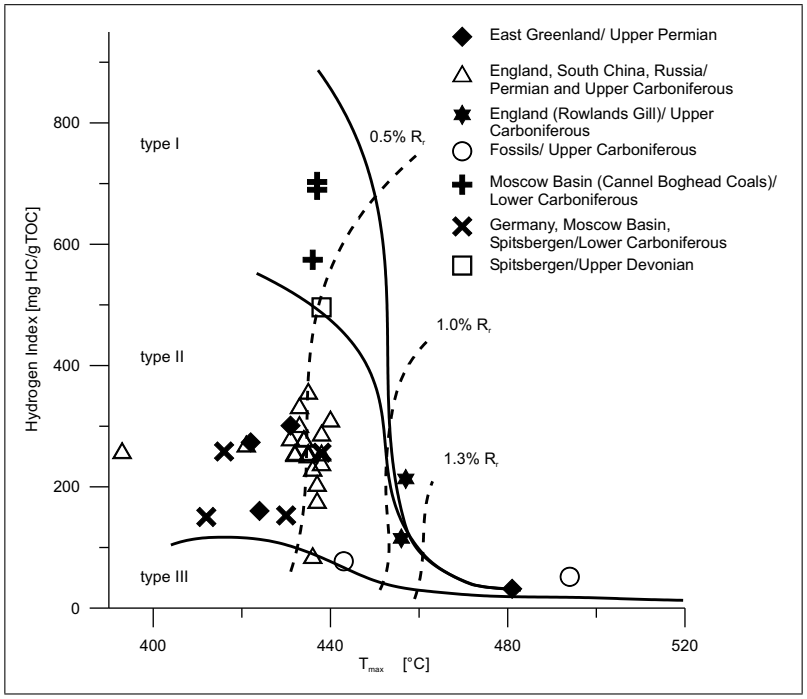

Figure 5.3: HI *vs.* T_{max} indicating a mixed type II-III kerogen for most of the samples

When interpreting data obtained by Rock-Eval pyrolysis some limitations have to be considered (Katz, 1983). While H/C and O/C ratios are established on pure kerogen, HI and OI base on the pyrolysis of the complete sediment. It was shown, that sediments containing high proportions of minerals release depleted amounts of volatile organic compounds. This can be caused by absorption of organic compounds onto the mineral matrix (Peters, 1986). This mineral matrix effect is normally accompanied by elevated T_{max} values. On the other hand breakdown of carbonates during pyrolysis may result in an enhanced OI (Katz, 1983).

OI values are low for most of the samples (Table A.2). In the HI *vs.* OI plot (Fig. 5.2) they are beneath the line for type I kerogen. Few values plot near that line. Only one sediment from East Greenland can be assigned to type III or perhaps type IV kerogen. The latter is not among the originally defined kerogen types (Tissot and Welte, 1984) due to its low reactivity and high proportions of inertinite macerals (Killops and Killops, 1993). The sample which has high OI values also has high amounts of minerals. Therefore Rock-Eval data of this sample may be influenced by a mineral matrix effect (Katz, 1983). Two sediments from

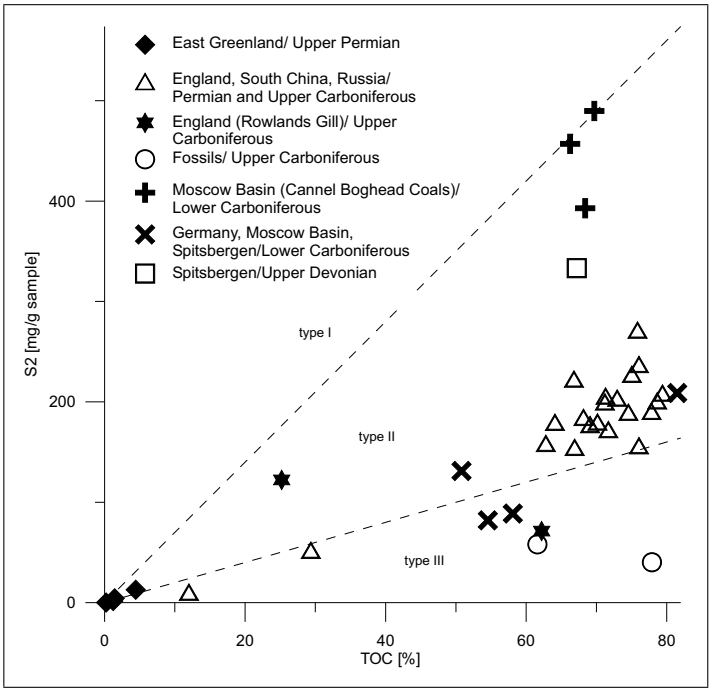

Figure 5.4: S2 *vs.* TOC graph supporting the distribution visualised in the HI *vs.* T_{max} graph

East Greenland can be assigned to mixed type II and III kerogen. These samples exhibit high proportions of minerals.

The cannel-boghead coals from the Viséan and the cannel coal from the Upper Devonian, according to the HI *vs.* OI plot, contain type I kerogen. However for most of the other samples the HI *vs.* OI plot is in clear contrast to their maceral group distribution (Fig. 5.1). Type I kerogen does not contain high proportions of vitrinite. Peters (1986) reported, that values of coals containing type III kerogen can lie between type II and III. This is caused by an overestimation of the liquid-hydrocarbon-generative potential. It especially was observed for coals showing maturities beyond 0.6% R_r. In these coals pyrolytic oxygen in high amounts is released as carbon monoxide, which is not detected by Rock-Eval. Nevertheless the very low OI values for most of the samples can not be explained by these facts and therefore may be of little significance. The HI values of 300 mg HC/ g TOC for most of them in contrast is typical for coals containing high amounts of type III organic matter (Peters, 1986).

According to the plot of HI *vs.* T_{max} (Fig. 5.3) most of the samples are classified as type II to type III kerogen. This is in good agreement to their maceral group

distribution (Fig. 5.1). The cannel-boghead coals and the cannel coal in this plot are assigned to contain type I to type II kerogen. The maturity of the samples according to the Rock-Eval data is low in comparison to the vitrinite reflectances determined via microscopy (Table A.1).

The comparison between the HI *vs.* OI (Fig. 5.2) and the HI *vs.* T_{max} plot (Fig. 5.3) strongly supports the suggestion that OI values are not reliable. Additionally the S2 *vs.* TOC plot (Fig. 5.4) correlates well to the data of the HI *vs.* T_{max} plot. The S2 *vs.* TOC plot was established by Langford and Blanc-Valleron (1990) to avoid problems related to the S3 peak. According to this plot (Fig. 5.4) the fossils and four coals strongly correspond to type III kerogen. Due to the low amounts of TOC for the four sediments from East Greenland their organic matter composition is difficult to assign (Fig. 5.4). The cannel-boghead coals from the Viséan and the Upper Devonian cannel coal again are classified to contain type I kerogen.

According to both the HI *vs.* T_{max} and the S2 *vs.* T_{max} plot most of the samples contain organic matter that can be assigned to a mixture of type II and III kerogen. The cannel-boghead coals and the cannel coal show the same kerogen typing in all three plots. The Rock-Eval data for the sediments from East Greenland due to the low amounts of TOC are insecure.

6 Molecular Geochemical Results

6.1 Compound Class Distribution by Iatroscan

The relative proportions of aliphatic hydrocarbons, aromatic hydrocarbons and resins (i.e. nitrogen, sulphur and oxygen containing compounds) were investigated for all of the Upper Carboniferous samples, with two exceptions (Table A.3). Additionally Iatroscan was applied for three Permian samples from Southern France (Table A.3). Resins (NSO compounds) are generally the most abundant compound class for all samples (Fig. 6.1), ranging from 47 to 90%, and are significantly highest for the *Sigillaria*. Aromatic hydrocarbons normally are present in higher amounts than aliphatic hydrocarbons. They are abundant in the range of 5-41%. Aliphatic hydrocarbons are present in proportions from 1 to 37%. They are only significantly enriched in two of the samples from Southern France.

6.2 Aliphatic Hydrocarbons

Introduction

The geochemistry of aliphatic hydrocarbons was subject to intensive investigations in the past. Aliphatic hydrocarbons, including the so-called biomarkers, are often applied and provide useful information about the biological origin, the depositional environment and the maturity of organic matter (Peters and Moldowan, 1993). They are highly abundant in kerogen derived from marine sources, but less predominant in kerogen originating from terrestrial environments (Tissot and Welte, 1984).

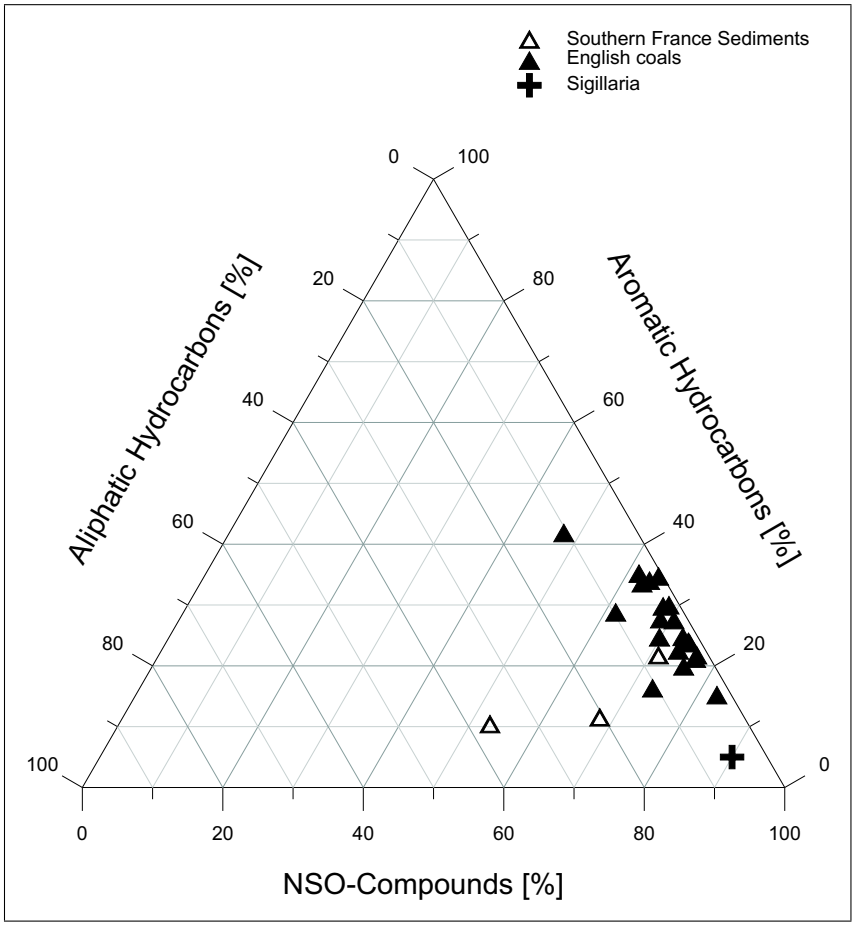

Figure 6.1: Ternary plot showing the relative amounts of aliphatic hydrocarbons, aromatic hydrocarbons and NSO compounds

Except for *n*-alkanes and pristane (2,6,10,14-tetramethylpentadecane), biomarkers often are rare in coals (Norgate *et al.*, 1999). Aliphatic by-products of decomposers may contribute the major part of biomarkers to the kerogen of terrestrial origin (Killops and Killops, 1993). Increasing maturity often results in aromatisation of cyclic aliphatic hydrocarbons. Therefore a depletion in the relative proportion of cyclic aliphatic hydrocarbons in samples of high maturity may additionally result in a more pronounced predominance of *n*-alkanes and pristane.

n-Alkanes

n-Alkanes are constituents of coals, sediments and petroleum (Killops and Killops, 1993). They provide information on the biological sources of the organic matter (Killops and Killops, 1993; Peters and Moldowan, 1993). In organisms they normally show odd numbers of C-atoms, due to their biosynthesis from fatty acids via enzymatic decarboxylation (Killops and Killops, 1993). *n*-Alkanes in the range from C_{27} to C_{31}, showing a clear odd over even predominance (OEP) are attributed to waxes of higher plants. Short-chain *n*-alkanes (C_{15} to C_{19}), exhibiting an OEP are presumed to originate from algae (Tissot and Welte, 1984).

The influence of different contributors to the distribution of *n*-alkanes can be expressed in ratios. The ATR_{HC} (aquatic/terrigenous ratio of hydrocarbons, Wilkes *et al.* (1999)) is a parameter to determine the amounts of aquatic to terrigenous derived *n*-alkanes, i.e. short-chain to long-chain *n*-alkanes :

$$ATR_{HC} = \frac{(C_{15} + C_{17} + C_{19})}{(C_{15} + C_{17} + C_{19} + C_{27} + C_{29} + C_{31})} \tag{6.1}$$

Values below 0.5 indicate an enhanced input of long-chain *n*-alkanes, i.e. organic matter derived from terrestrial sources. The ratio depends on the maturity of the samples and is only distinctive for immature organic matter.

Samples of low maturity normally show the biogenic distribution of *n*-alkanes. This predominance of odd- over even-numbered *n*-alkanes becomes less pronounced with increasing maturity of the organic matter. Due to thermal cracking an increase of short-chain *n*-alkanes is observed, leading to equal proportions of odd- and even- numbered *n*-alkanes (Killops and Killops, 1993). Several ratios reflecting the OEP of *n*-alkanes are known (Peters and Moldowan, 1993). The CPI (carbon preference index) used in this study is often applied (Norgate *et al.*, 1999; Wilkes *et al.*, 1999) and takes the distribution of $C_{(24-32)}$ *n*-alkanes into consideration:

$$CPI_{LHC} = \frac{1}{2}\left(\frac{(C_{25} + C_{27} + C_{29} + C_{31})}{(C_{24} + C_{26} + C_{28} + C_{30})} + \frac{(C_{25} + C_{27} + C_{29} + C_{31})}{(C_{26} + C_{28} + C_{30} + C_{32})}\right) \tag{6.2}$$

The ATR_{HC} is only reliable for CPI values significantly higher than one.

The amounts of summed $C_{(12-32)}$-*n*-alkanes range from 23 to 6080 μg/g TOC (Table A.5). *n*-Alkanes, besides pristane normally are the most abundant compounds of the aliphatic fraction (Fig. 6.2). They are significantly enriched for the more immature samples, characterised by high proportions of liptinite. They are lowest for samples showing enhanced maturities. Most of the samples in the maturity range of 0.72-0.91% R_r show proportions of *n*-alkanes at around 500-700 μg/g TOC.

An unimodal distribution (Fig 6.2 A, C), maximising around *n*-$C_{(21-25)}$ (Fig. 6.2 C) characterises most of the fractions of aliphatic hydrocarbons. Only few of the immature samples show a clear predominance of long-chain odd-numbered *n*-alkanes (Fig. 6.2 B). The values of the carbon preference index (CPI) normally range from 1.03 to 1.66 (Table 6.1), indicating, that organic matter for most of the samples is mature. Low CPI values for samples of maturities beyond 0.6% R_r are in good agreement with data from the literature (Radke *et al.*, 1980; Norgate *et al.*, 1999). Only two samples exhibit a clear OEP, typical for immature organic matter (Table 6.1). In contrast, samples that are also characterised by low maturities (Table 5.1, confirmed by high HI-values (Table A.2)) show CPI-values, that are only slightly enhanced.

One sample exhibits an even over odd predominance (EOP) of *n*-alkanes, this being characteristic for strongly reducing, hypersaline environments (Peters and Moldowan, 1993).

The values for ATR_{HC} vary widely (Table 6.1). Their significance is limited according to the low CPI-values. The ATR_{HC} is low for samples that show a CPI higher than 1.6 (Table 6.1). This may indicate a strong contribution of cuticular waxes from higher plants to the organic matter of these samples. The CPI of the *Sigillaria* is in contrast to its enhanced maturity (Table 6.1).

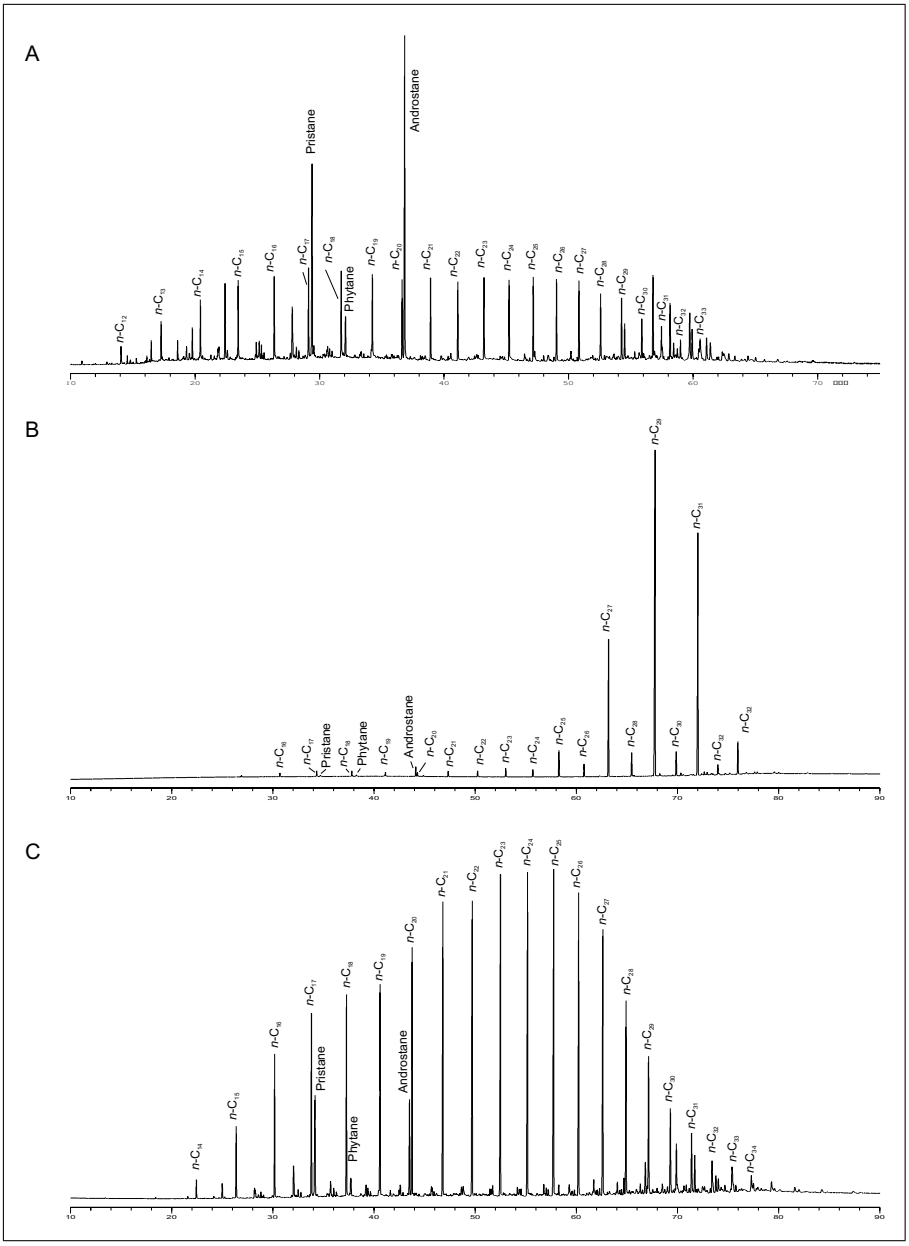

Figure 6.2: Gas chromatograms of the aliphatic hydrocarbon fraction of samples from A) the Westphalian (England) B) the Viséan (Russia) and C) the Devonian (Spitsbergen); androstane was added as internal standard

Table 6.1: CPI- and ATR_{HC}-values of the samples

Sample	CPI_{HC}	ATR_{HC}	Sample	CPI_{HC}	ATR_{HC}
E 49710	1.21	0.38	E 48395	1.24	0.98
E 49748	1.15	0.47	E 48394	1.21	0.56
E 49749	1.39	0.16	E 48396	1.15	0.54
E 49750	1.11	0.75	E 48397	1.12	0.58
E 49751	1.08	0.35	E 48398	1.13	0.49
E 48990	1.04	0.50	E 48400	1.23	0.49
E 48478	1.08	0.60	E 48401	1.17	0.58
E 48479	1.33	0.56	E 48405	1.27	0.90
E 48480	n.d	n.d	E 48425	1.66	0.21
E 48996	1.63	0.03	E 48382	1.11	0.41
E 48388	1.14	0.35	E 48383	1.17	0.51
E 48389	1.14	0.56	E 48384	1.08	0.71
E 48390	1.13	0.65	E 48985	1.35	0.29
E 48214	1.11	0.62	E 48986	1.41	0.24
E 48216	1.17	0.54	E 48987	1.45	0.24
E 48430	1.34	0.58	E 48988	0.92	0.74
E 48403	1.17	0.58	E 48989	12.11	0.01
E 48220	1.07	0.64	E 48993	3.45	0.02
E 48392	n.d.	n.d.	E 48991	1.19	0.33
E 48393	1.09	0.56	E 48992	1.08	0.46

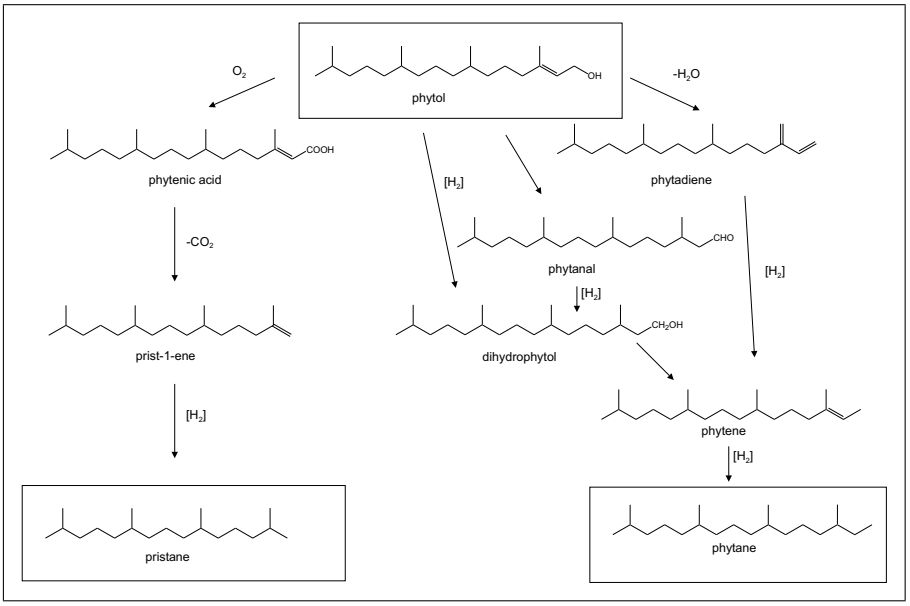

Figure 6.3: Formation of pristane and phytane from phytol

Pristane and Phytane

Pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane) originate from the phytol side chain of chlorophyll-a. Chlorophyll is a tetrapyrrole pigment, required for photosynthesis by higher plants, cyanobacteria and algae (Killops and Killops, 1993). Chlorophyll-a is the most abundant tetrapyrrole. Phytol additionally is present in bacteriochlorophyll-a and -b. It is released from tetrapyrrole pigments during diagenesis (Peters and Moldowan, 1993). Pristane and phytane normally are the most abundant isoprenoids in the aliphatic hydrocarbon fraction (Peters and Moldowan, 1993). Whereas pristane is derived by oxidation and decarboxylation of phytol, phytane is the product of its dehydration and reduction (Fig. 6.3).

The ratio of pristane to phytane is used as an indicator of the redox potential in sediments. At maturity ranges of 0.65 to 1.3% R_r, values beyond 3 indicate an input of terrestrial derived organic matter deposited under oxic conditions. Values below 0.6 indicate anoxic, hypersaline environments. Values in the range of 0.8-2.5 are less significant and may indicate a lacustrine or marine origin of organic matter (Peters and Moldowan, 1993). The ratio is not sensitive to organic matter

of low maturities (Volkman and Maxwell, 1986). The ratio of pristane *vs.* *n*-C_{17} is another useful tool to characterise the source of organic matter. Values beyond 0.6 are attributed to organic matter derived from terrestrial sources. Values below 0.5 indicate, that organic material has derived from marine sources (Peters and Moldowan, 1993).

Pristane and phytane are present in the range from 1.4 to 172 μg/g TOC and 0.5 to 97 μg/g TOC (Table A.7), respectively. For the majority of the samples pristane is present in higher proportions than phytane (Table 6.2). The values of pristane *vs.* phytane indicate, that the Upper Carboniferous samples have been deposited under oxic conditions, and that organic matter except for one sample is mainly derived from terrestrial sources. The organic matter in most of the samples of the Permian and Viséan period on the other hand, according to the ratio, originates from lacustrine or marine sources. The immature samples of the Viséan exhibit values below 1. This may indicate, that depositional conditions have been primarily anoxic. In contrast to the ratio of pristane *vs.* phytane, the ratio of pristane *vs.* *n*-C_{17} indicates, that input of terrestrial organic matter is high for most of the samples (Table 6.2). Only few samples show values below 0.6. None of them is characterised by pristane/phytane ratios higher than 3.0. Therefore their organic matter may mainly be derived from marine sources.

Steranes and Diasteranes

Sterols (Fig. 6.4) are the natural precursors of steranes and diasteranes (de Leeuw and Baas, 1986). They are components in cell membranes, that serve to maintain the membrane integrity (Killops and Killops, 1993). Sterols naturally show a 8β(H),9α(H), 10β(CH_3),13β(CH_3),14α(H),17α(H),20*R*-configuration.

Whereas sterols originating from algae possess rather complex structures, the ones biosynthesized by higher plants are relatively simple. The variability of their side-chain structures is limited (Djerassi *et al.*, 1979; Djerassi, 1981). Sterols are present as free and esterified compounds in nature. It is believed, that the initial step of biotransformation is the hydrolysis of the esterified derivatives (de Leeuw and Baas, 1986). During diagenesis sterols undergo transformations, that result in

Table 6.2: Values of pristane/phytane and pristane/n-C_{17}

Sample	$\frac{pristane}{phytane}$	$\frac{pristane}{n\text{-}C_{17}}$	Sample	$\frac{pristane}{phytane}$	$\frac{pristane}{n\text{-}C_{17}}$
E 49748	1.27	2.54	E 48394	4.90	4.43
E 49749	1.16	1.47	E 48395	1.27	0.24
E 49750	1.71	0.92	E 48396	4.36	3.26
E 49751	1.66	2.50	E 48397	2.89	0.66
E 49710	6.81	3.41	E 48398	3.68	2.46
E 48990	2.91	1.11	E 48400	4.33	2.76
E 48478	1.22	0.67	E 48401	4.83	2.28
E 48479	1.33	0.50	E 48405	2.34	0.46
E 48480	0.21	0.47	E 48425	1.13	0.81
E 48996	3.33	5.56	E 48382	5.61	3.65
E 48388	3.49	3.70	E 48383	5.41	5.66
E 48389	4.62	2.88	E 48384	2.27	0.17
E 48390	5.40	2.65	E 48985	0.49	0.74
E 48214	5.07	2.16	E 48986	0.97	0.37
E 48216	5.32	4.73	E 48987	0.82	0.16
E 48430	6.28	2.26	E 48988	0.59	0.84
E 48403	3.44	1.37	E 48989	0.81	0.45
E 48220	5.08	2.77	E 48993	3.06	1.29
E 48392	n.d.	n.d.	E 48991	3.38	0.63
E 48393	4.45	2.99	E 48992	4.75	0.80

the formation of steranes and diasteranes (Brassell, 1985). The most likely direct precursors of steranes and diasteranes are sterenes and diasterenes, respectively (de Leeuw and Baas, 1986). The saturated isomers are the result of hydrogenation. The ratio of diasteranes to steranes provides information about the presence of minerals. The formation of diasteranes and their unsaturated counterparts, the diacholestenes results from rearrangement processes, catalyzed by certain clay minerals under acidic conditions (Rubinstein *et al.*, 1975; Sieskind *et al.*, 1979). The relative proportions of diasteranes do not depend on the total amount of clay minerals, but on the relative proportion of clay minerals to the proportion of organic matter (van Kaam-Peters *et al.*, 1998). This effect becomes less distinctive with increasing maturity of the samples (Inaba *et al.*, 2001). At elevated matura-

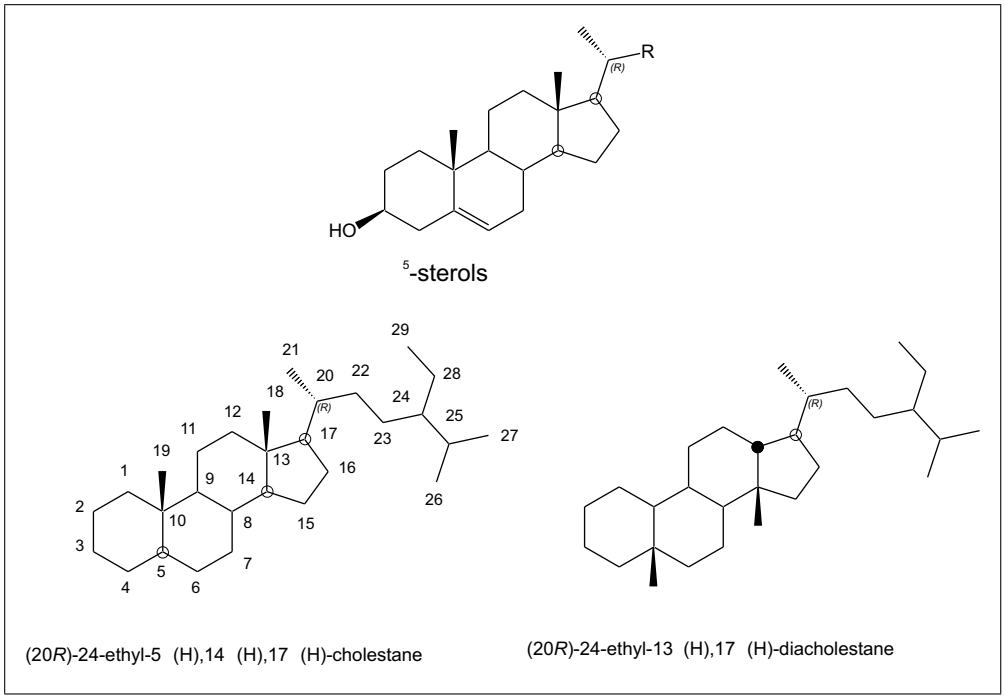

Figure 6.4: Steroid compounds referred to in the text

tion stages enhanced proportions of diasteranes can be attributed to their greater thermal stability. Furthermore diasteranes are less susceptible to biodegradation than regular steranes (Seifert and Moldowan, 1979).

The relative proportions of C_{27}-, C_{28}- and C_{29}-steranes and diasteranes to some extend provide information on the origin of the organic matter (Peters and Moldowan, 1993). Whereas C_{29}-steranes are suggested to predominantly originate from higher plants, C_{28}-steranes are supposed to originate from phytoplankton (Huang and Menschein, 1979). Isomerisation at the double bond of sterenes and diasterenes yields in an equilibrium mixture of different isomers. During diagenesis and catagenesis isomerisation at the C-5, C-14, C-17 and C-20 atoms of the sterane skeleton results in an equilibrium mixture of $\alpha\alpha\alpha R$, $\alpha\alpha\alpha S$, $\alpha\beta\beta R$, $\alpha\beta\beta S$-steranes at about 1:1:3:3 (Peters and Moldowan, 1993).

Steranes and diasteranes were trace compounds in the aliphatic hydrocarbon fractions of few samples, only. For many samples $\alpha\alpha\alpha R$ C_{27}-, C_{28}- and C_{29}-steranes were the only detectable steranes (Table A.10). In correspondence, these samples often are characterised by relatively low maturities. Diasteranes on the other hand

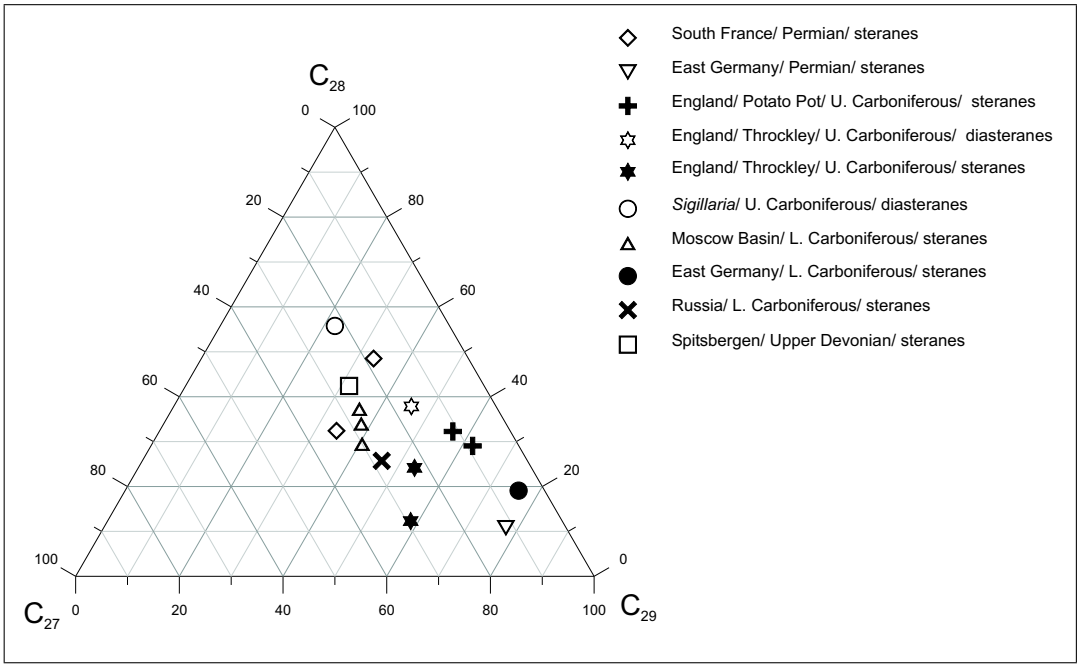

Figure 6.5: Ternary plot showing the relative proportions of C_{27}-, C_{28}- and C_{29}-steranes and diasteranes

are predominant in some of the more mature samples and in few samples that exhibit enhanced proportions of clay minerals (Table A.10). Maturity ratios based on the relative proportions of different sterane isomers, due to the low proportions of these compounds could only be determined for five samples (Table A.12). These values are of little significance and it is concluded, that the low proportions of steranes and diasteranes result in an enhanced inaccuracy of quantification. $\alpha\alpha\alpha R$-C_{29}-Steranes and $\beta\alpha S$-C_{29}-diasteranes often are the most abundant isomers (Fig. 6.5), indicating a contribution of land plant derived material to the organic matter of the samples. This conclusion is limited by the fact, that high proportions of C_{29}-steranes have also been found in samples characterised by the absence of land plant derived organic matter (Peters and Moldowan, 1993). Nevertheless the predominance of C_{29}-steranes is significant for the two German samples (Fig. 6.5). The relative amounts of C_{27}- and C_{28}-isomers do not vary significantly, showing a slight predominance C_{28}-steranes/diasteranes, only.

The ratio of diasteranes to steranes could be established for five samples only (Table A.12). A direct correlation between the ratio of clay minerals to organic

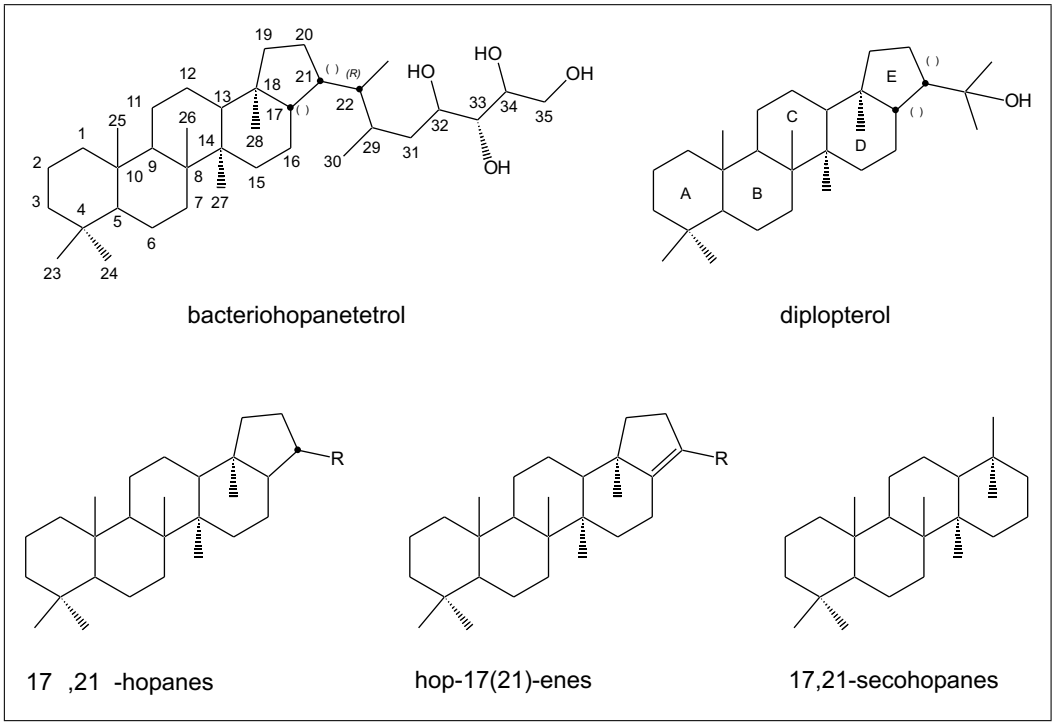

Figure 6.6: Hopanoic compounds referred to in the text

matter and the relative proportions of diasteranes was not observed. The Devonian cannel-coal is the only sample, which is characterised by an enhanced influence of acidic clays on the sterane/diasterane distribution.

Hopanes

The name hopane refers to a group of aliphatic biomarkers consisting of a pentacyclic terpenoic skeleton, incorporating a five membered E-ring (Fig. 6.6). Hopanes in the range of C_{27} to C_{35} are present in sediments, petroleum and coals (Simoneit, 1986). They originate from natural precursors like C_{35}-bacteriohopanetetrol and related C_{30}- or C_{35}-bacteriohopanoids (Fig. 6.6), which are constituents of cell membranes in a great range of bacteria (Ourisson *et al.*, 1979, 1987). These compounds are the counterparts of sterols, the latter being present in eukaryotes (Ourisson *et al.*, 1987).

Hopanes possess a chiral center at all ring junctures (C-5, C-8, C-9, C-10, C-13, C-17 and C-18) and at the C-21 and C-22 atoms. The biological hopane precursors show a 17β(H),21β(H),22R-configuration. In sediments three isomeric series, 17α(H),21β(H)-, 17β(H), 21β(H)- and 17β,21α(H)-hopanes, are present. The latter compounds are called moretanes. The presence of different isomers results from a great number of complex reactions, including isomerisation, destruction and release from kerogen (ten Haven *et al.*, 1992; Requejo, 1994).

Hopanes and their biological precursors were extensively studied for some decades. Although their transformation pathways during diagenesis and catagenesis are not fully understood (Farrimond *et al.*, 1996, 2000), they are often applied for both maturity and environmental assessment (Peters and Moldowan, 1993). High values for the ratio of C_{35}-/C_{31-35}-hopanes (Table 6.3, HHI=homohopane index) for example indicate highly reducing marine environments (Peters and Moldowan, 1991). In non-reducing environments bacteriohopanetetrol is oxidised to C_{32}-hopanoic acid. Loss of the carboxylic group results in enhanced proportions of C_{30}- and C_{31}-hopanes.

Maturity parameters based on hopanes normally consider the relative proportions of different isomers (Table 6.3). Isomerisation of naturally occurring 22R-homologues results in an equilibrium mixture of 22R- and 22S-isomers. Beyond maturities of 0.6% R_r an equilibrium value (0.6) is observed. The ratio of hopanes/(hopanes + moretanes) (Table 6.3) does also correspond to maturity (Table 6.3). At elevated maturity ranges the relative proportions of moretanes show a decrease.

Hopenes (Fig. 6.6), due to dehydrogenation possess a double bond in the pentacyclic skeleton (Tritz *et al.*, 1999). The most prominent hopenes are C_{30}-hop-17(21)-ene and its higher homologues (Summons and Jahnke, 1992; Gallegos, 1981). The relative proportions of hop-17(21)-enes decrease with increasing maturities.

Another compound class, that may be related to hopanes are tetracyclic terpanes. In contrast to hopanes, they lack the presence of the five membered E-ring. Tetracyclic terpanes have been detected in sediments and petroleum (Aquino Neto *et al.*,

Table 6.3: Selected parameters reflecting the proportions of different hopane isomers

Name	Formula	Significance
HHI	$\frac{C_{35}}{C_{31}+C_{32}+C_{33}+C_{34}+C_{35}}$	environment
$\frac{22S}{22S+R}$	$\frac{22S\text{–}17\alpha(\mathrm{H}),21\beta(\mathrm{H})\text{-29-Dihomohopane}}{22S\text{–}+R\text{–}17\alpha(\mathrm{H}),21\beta(\mathrm{H})\text{-29-Dihomohopane}}$	maturity
$\frac{Hopane}{Hopane+Moretane}$	$\frac{17\alpha(\mathrm{H}),21\beta(\mathrm{H})\text{-Hopane}}{17\alpha(\mathrm{H}),21\beta(\mathrm{H})\text{-Hopane}+17\beta(\mathrm{H}),21\alpha(\mathrm{H})\text{-Hopane}}$	maturity

1983). They are called 17,21-secohopanes, refering to the fact, that they may originate from hop-17(21)-enes via cleavage of the 17(21)-bond. These tetracyclic terpanes are absent in recent sediments and are suggested to be more resistant against biodegradation and maturity effects than hopanes (Aquino Neto *et al.*, 1983).

Hopanes have been assigned by mass spectra and literature. Their proportions and composition vary widely. They have not been identified in all of the investigated samples. When determined, summed hopanes were present in ranges from 3.3 to 317.1 μg/g TOC (Table A.14). Proportions of hopanes were relatively enhanced for most of the immature samples, but exhibit no uniform decrease with increasing maturities. Whereas the hopanoic compounds for most of the samples are restricted to few isomers only, four immature samples show a high diversity. For the majority of the samples 17α-22,29,30-trinorhopane, 17α(H),21β(H)-hopane and 17α(H),21β(H)-norhopane are the most abundant isomers. While C_{35}-hopanes were generally absent, isomers with up to 34 carbon atoms were present. Additionally in comparison with Summons and Jahnke (1992) a 2- or 3-methyl-hopane was also detected in few of the samples. Due to the absence of C_{35}-hopanes the HHI could not be determined. However, the absence or negligible proportions of

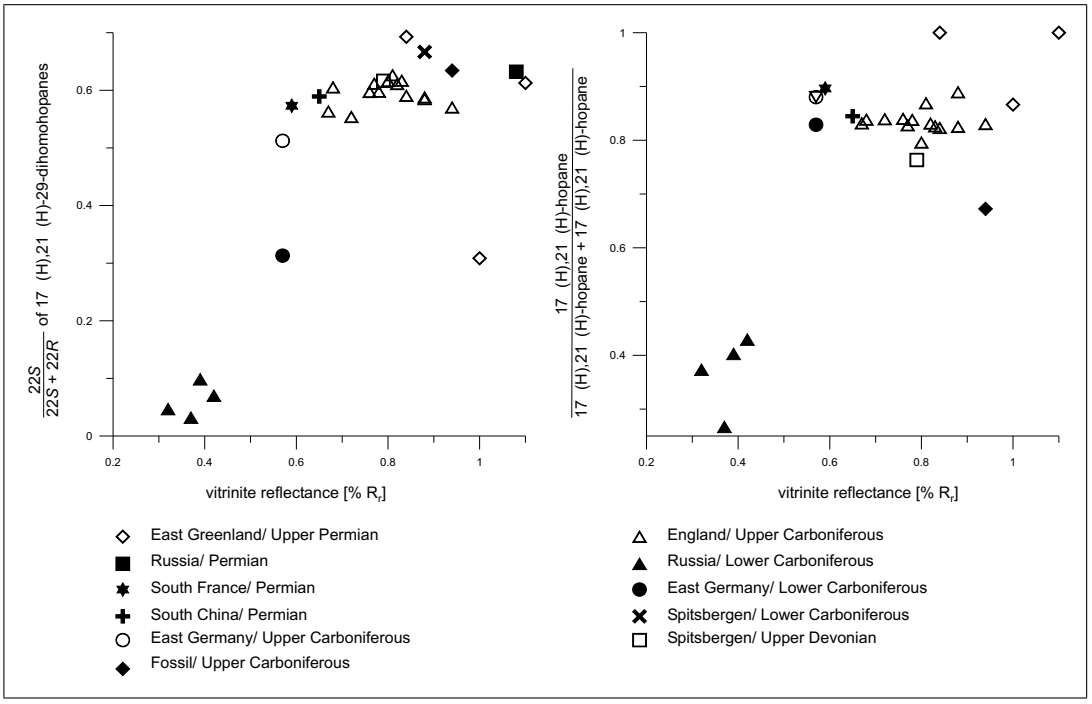

Figure 6.7: A) Cross plot of the distribution of 22*S* and 22*R* 17α,21β-homohopanes and B) of C_{32}-17α,21β-hopanes and moretanes *vs.* the vitrinite reflectance of the samples

these higher homologues indicate, that the environmental conditions for none of the samples have been strongly anoxic.

Maturity parameters basing on the relative proportions of different isomers, show a correlation to the vitrinite reflectance of the samples (Fig. 6.7). The equilibrium value for the ratio of $\frac{22S}{22S+R}$ 17α-dihomohopanes is reached for most of the samples (Fig. 6.7 A). This is in good agreement with the applicability of the ratio up to maturities of 0.6% R_r. One sample of the Permian in East Greenland exhibits a low ratio in contrast to its vitrinite reflectance (Fig. 6.7 A). The ratio of C_{30}-17α(H),21β(H)-hopanes to C_{30}-moretanes also exhibits good correlation to vitrinite reflectances (Fig. 6.7 B).

Hop-17(21)-enes, in the range from C_{29}- to C_{35} have only been detected in four immature samples originating from the Moscow Basin. They are absent in samples with maturities beyond 0.5% R_r. The higher homologues ($C_{(31-35)}$) are present as *R* and *S* isomers (Sinninghe Damsté *et al.*, 1995). The presence of $C_{(31-35)}$-hop-17(21)-enes correlates to the presence of 17β(H),21β(H)-hopane. This indicates,

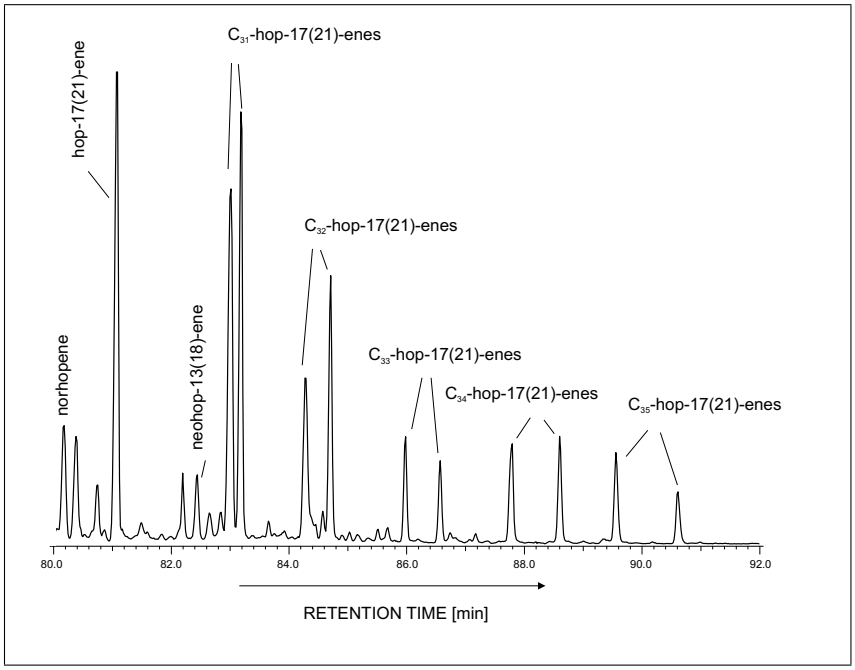

Figure 6.8: Gas Chromatogram of hopenes (m/z 396,410,424,438,452,466,480) in a sample from the Moscow Basin

that the compounds are of enhanced thermal instability. The homohop-17(21)-ene index (Table A.16) is low, this being in good agreement with the absence of C_{35}-hopanes. The relative proportions of *R*- and *S*-isomers are similar for all four samples. A slight predominance of the *R*-isomer is observed for lower homologues of the hop-17(21)-ene series, only (Table A.16).

Up to five tetracyclic C_{24-26}-17,21-secohopanes have been detected (Table A.17). Besides one C_{25}- two C_{24}- and two C_{26}-tetracyclic terpanes are present. While one C_{24}- and one C_{25}-isomer are present in most of the samples, the presence of other compounds is restricted to fewer samples.

Resumée

The fraction of aliphatic hydrocarbons for most of the samples is dominated by *n*-alkanes. Only one sample shows a strong OEP, whereas most of the samples show no significant predominance of odd-numbered *n*-alkanes. This does also account for samples, that are suggested to have suffered little thermal alteration.

The ratio of pristane/phytane shows enhanced values for most of the Upper Carboniferous samples. The samples from the Moscow Basin in contrast are characterised by pristane/phytane values below one, whereas most of the Permian samples show values in the range of 1-2.

The values of pristane/*n*-C_{17} for most of the samples support the suggestion, that their organic matter is derived from terrestrial sources. In contrast to the generally low pristane/phytane values for the samples of the Moscow Basin, their values of pristane/*n*-C_{17} vary more widely.

Steranes and diasteranes in general are minor constituents of the fractions of aliphatic hydrocarbons. Nevertheless two samples, characterised by an elevated CPI_{LHC} and a low ATR_{HC} show high proportions of C_{29}-steranes/diasteranes. Other samples show no significant variations of steranes and diasteranes. This probably results from the low proportions of these compounds.

Hopanoic compounds are present in higher amounts than steranes. This is indicative for a strong input of terrigenous organic material (Peters and Moldowan, 1993). Whereas the variability of different hopane-isomers is low for most of the samples, this does not account for the ones from the Moscow Basin. These samples, with one exception show an enhanced variability of different isomers. The ratio of $22S/(22S + 22R)$-17α(H),21β(H)-29-dihomohopanes is in excellent correlation to data from literature, except for one sample (Peters and Moldowan, 1993). The proportions of C_{30}-17α(H),21β(H)-hopanes to C_{30}-moretanes in contrast are of depleted significance, they show weaker correspondence to vitrinite reflectances. While hop-17(21)-enes were present in the immature samples from the Moscow Basin only, 17,21-secohopanes are present in an elevated number of samples. However few isomers are predominantly present in organic matter originating from the Devonian and Lower Carboniferous.

6.3 Aromatic Hydrocarbons

Introduction

Terrestrial organic matter, especially in coals, in comparison to organic matter derived from marine sources, normally is characterised by high proportions of aromatic hydrocarbons (Tissot and Welte, 1984). Many of the precursors originating from higher plants show either cyclic or already aromatic structures. Additionally aromatisation, besides defunctionalisation is the main chemical reaction occurring during coalification i.e. maturation of coals. Increasing maturity therefore is accompanied by an increase of compounds showing non-functionalised aromatic structures (Hazai *et al.*, 1989; Teichmüller and Teichmüller, 1968).

Investigations on brown coals (Hazai *et al.*, 1989; Chaffee and Fookes, 1988; Chaffee and Johns, 1983) showed that pentacyclic monoaromatic ring systems were highly abundant, whereas bi- and tricyclic polyaromatic rings (alkylnaphthalenes and -phenanthrenes) were absent. In contrast to this, bituminous coals, i.e. more mature coals normally are characterised by high proportions of alkylphenanthrenes and alkylnaphthalenes (Radke *et al.*, 1990; Hayatsu *et al.*, 1978b).

The presence of aromatic hydrocarbons in the extractable organic matter can result either from the aromatisation of free non-aromatic biogenic precursor molecules, for example retene derived from abietic acid (Radke *et al.*, 1982b) or from fragmentation of the polymeric coal matrix leading to the release of aromatic hydrocarbons at elevated maturities (Borwitzky and Schomburg, 1979). Additionally aromatic hydrocarbons, especially polyaromatic hydrocarbons (PAHs) are products of combustion. They are introduced into the organic matter during or before early diagenesis (Radke *et al.*, 1982a).

Increasing yields of aromatic hydrocarbons, incorporating 11 or more carbon atoms are observed at vitrinite reflectances in the range of 0.7-0.9% R_r. Beyond that stage a stepwise decrease in yields up to maturities of 1.1% R_r has been noticed (Radke *et al.*, 1990; Hayatsu *et al.*, 1978b).

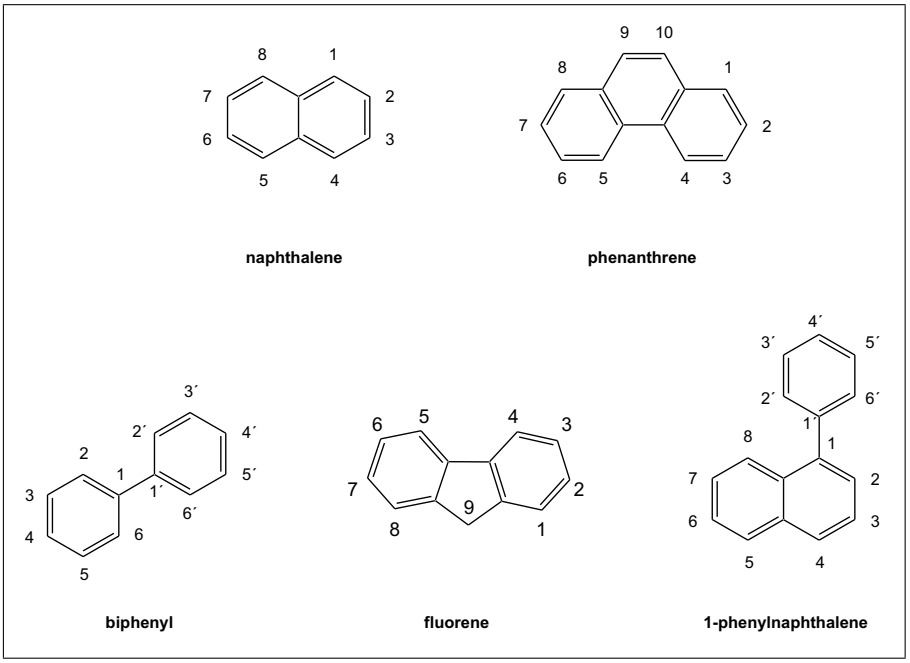

Figure 6.9: Aromatic compound classes present in the samples and their ring numbering conventions

Within the aromatic hydrocarbon fractions of the investigated samples alkylnaphthalenes and alkylphenanthrenes have been the most abundant compound classes and will be discussed in detail. Additionally alkylbiphenyls, alkylfluorenes and alkylphenylnaphthalenes have been minor contributors to the fraction. Due to their relative low abundances and little variations only a brief overview will be given.

Naphthalene and Alkylnaphthalenes

Alkylnaphthalenes are mainly derived from terrestrial sources (Radke *et al.*, 1994); several precursors are known:

- cyclic sesquiterpenoids, derived from resinous constituents of conifers are potential precursors of alkylnaphthalenes (Pentegova *et al.*, 1968),

- thermal degradation of β-carotene (Fig. 6.10) led to the formation of 2,6-dimethylnaphthalene, 1- and 2-methylnaphthalene and naphthalene (Day and Erdman, 1963; Achari *et al.*, 1973),
- 1,6-dimethyl-4-isopropylnaphthalene (cadalene) is a possible depolymerisation and aromatisation product of polycadinenes (van Aarssen *et al.*, 1990, 1992), and is produced via thermal treatment of farnesol (Douglas and Mair, 1965),
- 1,2,7-trimethylnaphthalene (1,2,7-TMN) is suggested to originate from compounds like β-amyrin (Fig. 6.11), that are constituents of angiosperms (Strachan *et al.*, 1988),
- β-amyrin and monoaromatic seco-hopanes are among several potential precursors of 1,2,5-trimethylnaphthalene and 1,2,5,6-tetramethylnaphthalene (1,2,5,6-TeMN)(Püttmann and Villar, 1987),
- 1,2,4-trimethylnaphthalene might originate from α-tocopherol, present in recent marine sediments (Brassell and Eglington 1986),
- 1,2,2,5-tetramethyltetralin and 1,2,2,5,6-pentamethyltetralin, from microbial sources, might be precursors of 1,2,6-trimethylnaphthalene, 1,2,5,7- and 1,2,3,5-tetramethylnaphthalene (Alexander *et al.*, 1992).

Some alkylnaphthalenes have various potential biological sources. Strachan *et al.* (1988) found high proportions of 1,2,5- and 1,2,7-trimethylnaphthalene in sediments from the Cretaceous and younger. The authors assumed, that these compounds are degradation products of pentacyclic triterpenoids of the oleanane-type, for example β-amyrin. The degradation of β-amyrin via 8,14-seco-triterpenoids (Fig. 6.11), is supposed to additionally yield in high proportions of 1,2,5,6-tetramethylnaphthalene (Püttmann and Villar, 1987). High proportions of 1,2,7-trimethylnaphthalene have been attributed to the presence of angiosperms in sediments (Fig. 6.11). In contrast 1,2,5-trimethyl- and 1,2,5,6-tetramethylnaphthalene may also derive from natural precursors showing a different structural constitution (Fig. 6.11). They may be formed via degradation of monoaromatic seco-hopanoids (Hussler *et al.*, 1984). Additionally both,

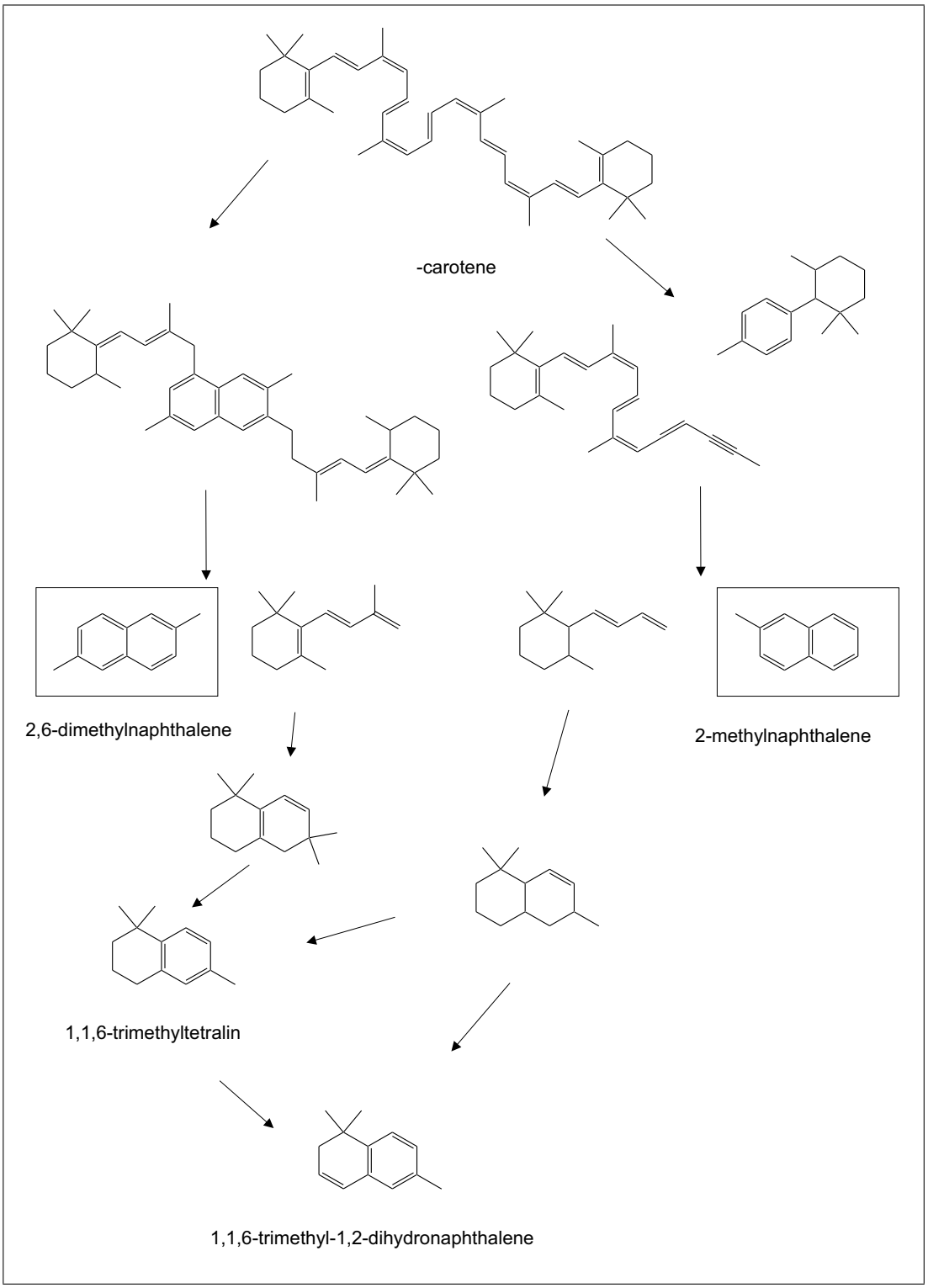

Figure 6.10: Suggested scheme for the pyrolytic degradation of β-carotene according to Achari *et al.* (1973)

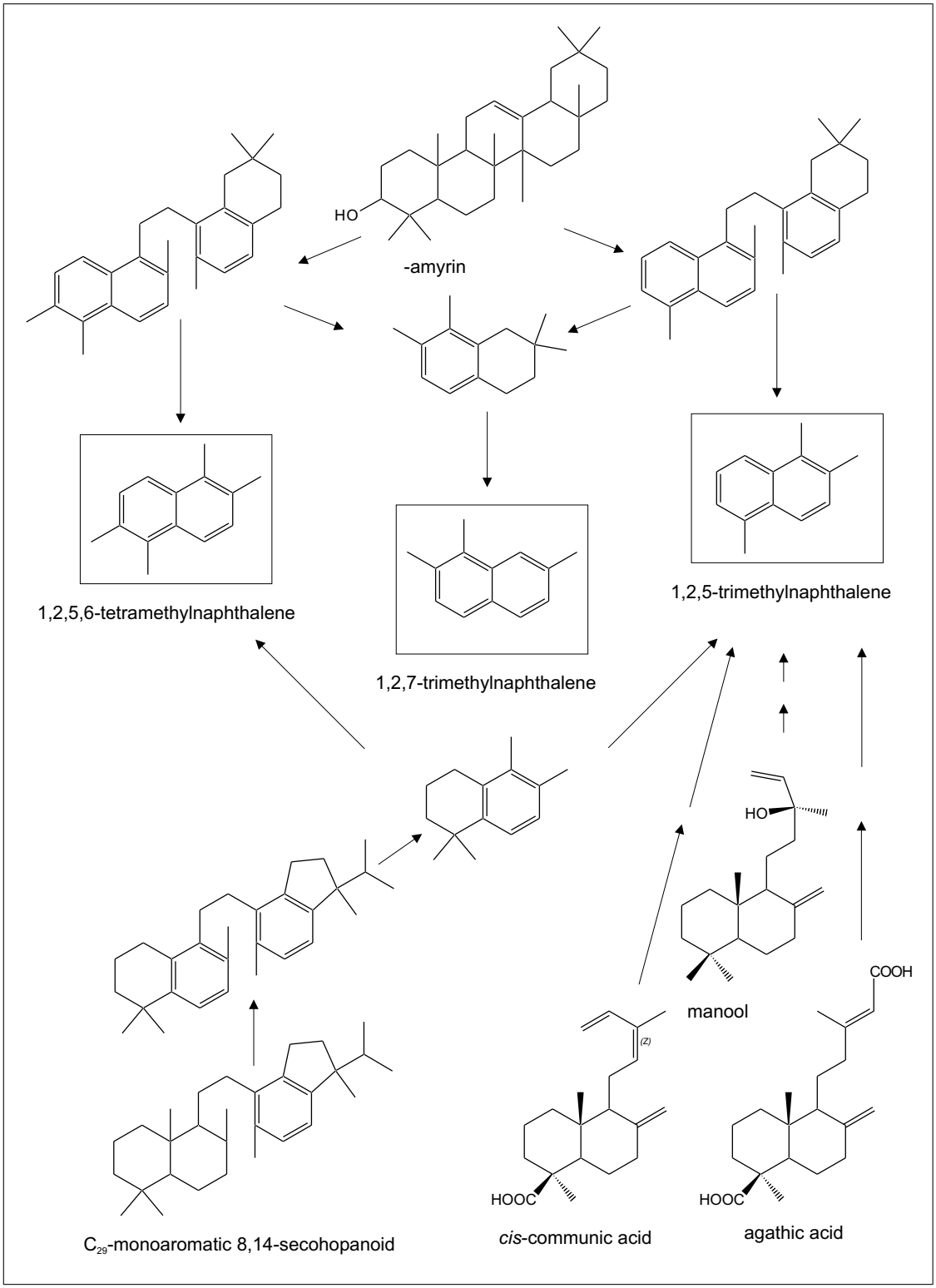

Figure 6.11: Possible precursors of 1,2,5,6-tetramethylnaphthalene, 1,2,7,- and 1,2,5-trimethylnaphthalene after Püttmann and Villar (1987) and Strachan *et al.* (1988)

1,2,5-trimethyl- and 1,2,5,6-tetramethylnaphthalene were detected as major constituents in the fluorinite filling of needles from *Abietites linkii*, a gymnosperm (Heppenheimer *et al.*, 1992). 1,2,5-Trimethylnaphthalene (agathalene) may also originate from the dehydrogenation of biological precursors (Fig. 6.11) like agathic acid, communic acid and manool (Thomas, 1969; Carman and Craig, 1971). The latter compounds are constituents of gymnosperms (Karrer, 1976; Thomas, 1969).

It has been mentioned that 1,6-dimethyl-4-isopropylnaphthalene (cadalene) is a product of thermal treatment of farnesol in the presence of sulphur. It was further assumed to be an aromatisation product of cadinane via depolymerisation of cadinenes and polycadinanes (Simoneit, 1986; van Aarssen *et al.*, 1990, 1992). While cadinenes are present in resins of higher plants and resinous material in conifers (Pentegova *et al.*, 1968; Heppenheimer *et al.*, 1992), polycadinenes originate from dammar resins of angiosperms. A biogenetic relationship between cadalene and 1,6-dimethylnaphthalene, as a possible by-product in the depolymerisation of polycadinenes has been suggested (van Aarssen *et al.*, 1992). However Radke *et al.* (1994) assumed other sources of 1,6-dimethylnaphthalene. High concentrations of this compound in immature sediments are unlikely to originate from cadinenes as aromatisation and depolymerization is supposed to require elevated thermal stress.

A series of isohexylalkylnaphthalenes has been identified in crude oils (Ellis *et al.*, 1996). The compounds were only abundant in crude oils that showed the presence of specific higher plant biomarkers. Ellis *et al.* (1996) suggested that these isohexylalkylnaphthalenes originate from resinous diterpenoids for example phyllocladanes via aromatisation and ring opening. The highest homologue of the series is 6-isopropyl-2-methyl-1-(4-methylpentyl)naphthalene (ip-iHMN).

To recognise source effects, Strachan *et al.* (1988) compared the relative amounts of 1,2,7- to 1,3,7-trimethylnaphthalene and the ones of 1,2,5- to 1,3,6-trimethylnaphthalene. While 1,2,7- and 1,2,5-trimethylnaphthalene are supposed to have direct biogenic precursors (Fig. 6.11), 1,3,7- and 1,3,6-trimethylnaphthalene are suggested to originate from the isomerisation of these two potential biomarkers. Although the two ratios depend on the maturity of the

Table 6.4: Maturity parameters based on the relative abundance of different alkylnaphthalenes

Name	Formula	Reference
MNR	$\frac{2-methylnaphthalene}{1-methylnaphthalene}$	Radke *et al.* (1982b)
ENR	$\frac{2-ethylnaphthalene}{1-ethylnaphthalene}$	Radke *et al.* (1982b)
DNR	$\frac{2,6-+2,7-DMN}{1,5-DMN}$	Radke *et al.* (1982b)
TNR1	$\frac{2,3,6-TMN}{1,3,5-+1,4,6-TMN}$	Alexander *et al.* (1986b)
TNR2	$\frac{1,3,7-+2,3,6-TMN}{1,3,5-+1,3,6-+1,4,6-TMN}$	Radke *et al.* (1986)
TNNr	$\frac{1,3,7-TMN}{1,3,7-+1,2,5-TMN}$	van Aarssen *et al.* (1999)
TeMN	$\frac{1,3,6,7-TeMN}{1,3,6,7-+1,2,5,6-TeMN}$	van Aarssen *et al.* (1999)
TrMN	$\frac{1,3,7-TMN+1,3,6-TMN+2,3,6-TMN}{\sum TMN}$	Kruge (2000)

samples, source effects are assumed to be recognisable, when establishing their logarithmic plot (Strachan *et al.*, 1988).

Besides these ratios reflecting source effects, the distribution of alkylnaphthalenes is supposed to be mainly influenced by the thermal history of organic matter in sediments. Increasing maturity for example results in the progressive conversion of 1,2,5-trimethylnaphthalene into the more stable 1,3,6-trimethylnaphthalene and other isomers (Strachan *et al.*, 1988). This results from isomerisation reactions, leading to the predominance of more stable β-isomers with increasing maturity. Several ratios based on the distributions of alkylnaphthalenes therefore compare the amounts of more stable to less stable isomers (Table 6.4).

The more stable β-isomers are substituted at position 2-, 3-, 6- and 7- of the naphthalene skeleton. Radke *et al.* (1982b) found, that samples of enhanced ma-

turity (>0,9% R_r) show elevated proportions of 2-methylnaphthalene compared to 1-methylnaphthalene. This does also account for the ratio of 2-ethylnaphthalene to 1-ethylnaphthalene (Table 6.4). Like the MNR and the ENR, the ratios of dimethylnaphthalenes (DNR) and trimethylnaphthalenes (TNR1 and TNR2) also increase with increasing maturity (Table 6.4). More recently van Aarssen *et al.* (1999) established ratios on the basis of laboratory experiments (Table 6.4). These experiments investigated the influence of thermal treatment on the distribution of alkylnaphthalenes in the presence of clay. The TrMN (Table 6.4) used by Kruge (2000) is a modification of the TNR2.

Investigations on the susceptibility of alkylnaphthalenes to microbial degradation showed that it depends on their substitution pattern. Naphthalenes characterised by a 1,6-substitution pattern are more susceptible to biodegradation than other isomers (Ahmed *et al.*, 1999). Furthermore dimethylnaphthalenes are more rapidly biodegraded than ethylnaphthalenes (Volkman *et al.*, 1984) and 2-ethylnaphthalene is preferentially degraded in comparison to 1-ethylnaphthalene (Ahmed *et al.*, 1999). In general the susceptibility of alkylnaphthalenes to biodegradation decreases with increasing number of methyl-substituents.

In the samples studied in this project naphthalene, methylnaphthalenes, ethylnaphthalenes, dimethylnaphthalenes, trimethylnaphthalenes, tetramethylnaphthalenes, cadalene and 6-isopropyl-2-methyl-1(4-methylpentyl)naphthalene (Fig. 6.12) were identified by retention indices, mass spectra and by literature (Alexander *et al.*, 1983; Rowland *et al.*, 1984). 1,8-Dimethylnaphthalene was used as an internal standard. Further alkylnaphthalenes, that were quantified, normally are minor contributors to the group (Fig. 6.12, Table A.18).

The absolute amounts of alkylnaphthalenes vary widely between 6 and 3228 μg/g TOC (Table A.18). Highest proportions were obtained within the maturity range of 0.80-0.88% R_r, except for two samples. Maturity parameters based on the distribution of alkylnaphthalenes, show no systematic dependence on the vitrinite reflectance of the samples (Table 6.5, Table A.18). An increase of the MNR within the maturity range of 0.6-1.5% R_r for example was not observed (Table 6.5). A predominance of 2-methylnaphthalene over 1-methylnaphthalene is significant for some of the most immature samples. On the other hand, some of the more ma-

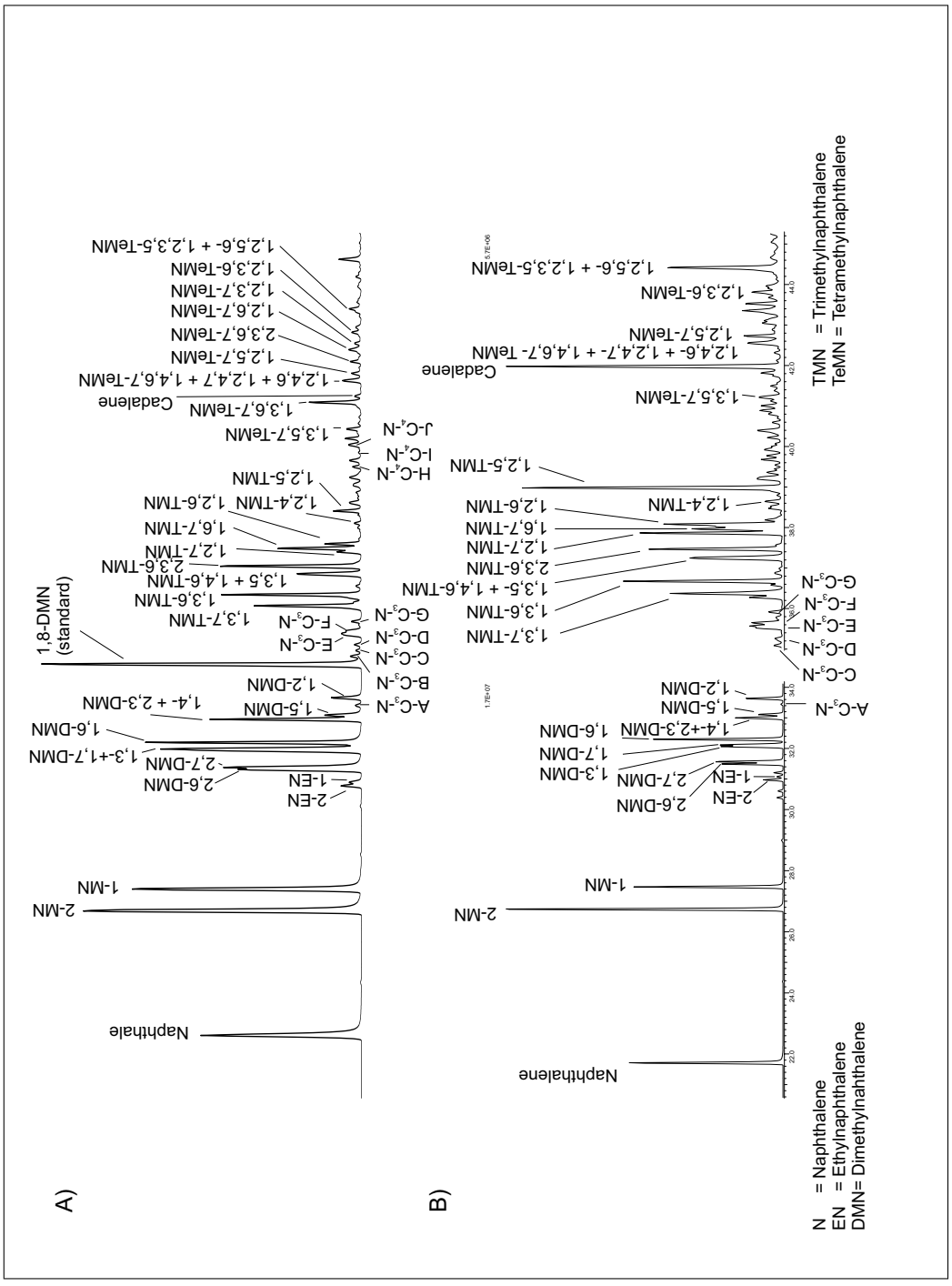

Figure 6.12: Gas Chromatogram (*m/z* 128, 142, 156, 170, 184, 198) of alkylnaphthalenes in A) an Upper Carboniferous and B) a Lower Carboniferous sample (for the latter sample, the chromatogram has been split due to the high proportions of the internal standard 1,8-dimethylnaphthalene)

Table 6.5: Values of selected alkylnaphthalene ratios; samples are listed in order of increasing maturity according to vitrinite reflectance (further ratios are listed in Table A.18)

Sample	MNR	ENR	DNR	Sample	MNR	ENR	DNR
E 48987	1.30	2.11	2.79	E 48216	1.38	1.16	4.49
E 48989	1.93	2.61	4.13	E 48394	0.28	0.86	4.09
E 48986	n.d.	1.88	2.68	E 48220	0.60	1.62	4.20
E 48985	n.d.	1.06	2.31	E 48388	1.24	1.13	4.22
E 48993	0.64	1.11	0.89	E 48390	1.67	1.35	5.54
E 48479	0.88	0.86	1.41	E 48991	1.08	1.30	2.48
E 49710	1.41	1.73	2.63	E 48383	0.78	1.15	2.44
E 48398	0.32	1.23	1.95	E 48389	1.47	1.27	5.44
E 48396	0.08	2.86	1.39	E 48384	1.46	1.19	2.74
E 48397	n.d.	0.47	2.30	E 48382	1.18	1.05	2.04
E 48393	0.59	0.99	3.03	E 48430	1.09	1.26	2.31
E 48992	0.94	0.87	1.34	E 49478	1.43	1.00	2.39
E 48401	0.39	0.56	1.61	E 48990	0.27	0.38	0.55
E 48400	0.59	1.08	2.69	E 49751	0.94	0.66	2.52
E 48395	0.50	4.41	3.77	E 48403	0.45	0.87	4.21
E 48214	1.40	1.30	4.52	E 48405	2.26	2.22	8.94

ture samples show relatively high proportions of 1-methylnaphthalene. A natural source of 2-methylnaphthalene, previously suggested by Borrego *et al.* (1997) may be the reason for its relatively high abundance in samples of low maturity. However this does not explain the enhanced proportions of 1-methylnaphthalene in some of the mature samples. The ENR is characterised by the same phenomenon (Table 6.5). High concentrations of 2-ethylnaphthalene compared to 1-ethylnaphthalene for the immature samples correspond to the high MN ratios of these samples (Table 6.5). The DNR correlates best with the maturity of the samples (Fig. 6.13). The ratio increases with increasing maturity for most samples at vitrinite reflectances in the range from 0.70 to 0.88% R_r. The Russian samples of low maturity again show relatively enhanced DN ratios in contrast to their vitrinite reflectance (Fig. 6.13). The Permian sample from Russia in contrast exhibits very low proportions of 2,6- and 2,7-dimethylnaphthalene considering its rather high maturity (Fig. 6.13). Whereas the DNR shows a slight correlation with vitrinite

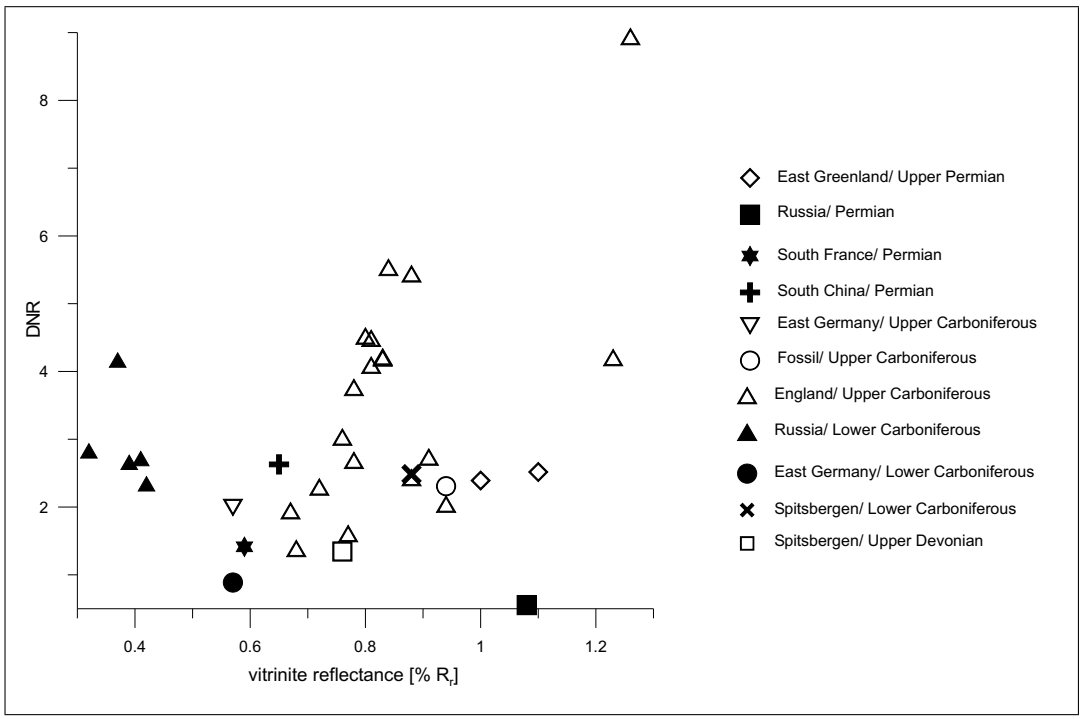

Figure 6.13: Cross plot of vitrinite reflectance *vs.* DNR

reflectance in the range of 0.70-0.88% R_r, this in any maturity range does not account for the TNR1, the TNR2 and further ratios (Table A.18).

Among the dimethylnaphthalenes, 1,6-dimethylnaphthalene often is highly abundant (Table A.18). The relative concentration shows no dependence on either age or maturity of the samples. Besides that, either 1,7- or 1,3-dimethylnaphthalene are major contributors to alkylnaphthalenes for many samples. The two compounds normally were not quantified separately. When quantified separately 1,7-dimethylnaphthalene is present in higher proportions (Table A.18). Enhanced concentrations of the two compounds in comparison to the amounts of summed 2,6- and 2,7-dimethylnaphthalene, even in samples of high maturity, contradict their depleted thermal stability (Budzinski *et al.*, 1993). The low concentrations of 1,5- and 1,2- dimethylnaphthalene in most of the samples on the other hand, can be attributed to their minor thermodynamic stability. However variations of individual compounds for different samples are weak.

In contrast to dimethylnaphthalenes, the distribution of trimethylnaphthalenes varies more widely. Normally 1,2,4-trimethylnaphthalene plays a minor role (Table A.18). 1,2,7-Trimethylnaphthalene, presumed to be an indicator of angiosperms, when highly abundant, shows relatively high proportions for some of the immature samples from the Viséan. 1,2,5-Trimethylnaphthalene often is a predominant compound. The relative proportion of 1,2,5-trimethylnaphthalene, in contrast to its low thermal stability (Budzinski *et al.*, 1993), is not significantly influenced by the maturity of the samples (Table A.18). Enhanced proportions of 2,3,6- and 1,3,6-trimethylnaphthalene for many samples of rather high vitrinite reflectances, correspond to the thermal stability of these isomers.

High concentrations of 1,2,5-trimethylnaphthalene often are accompanied by enhanced proportions of the 1,2,5,6- and 1,2,3,5-tetramethylnaphthalene which coelute. Like for 1,2,5-trimethylnaphthalene, their proportions show no significant depletion in samples of enhanced maturities. This is in contrast to suggestions made by Püttmann and Villar (1987), who suggested a recognisable decrease of the two potential biomarkers 1,2,5-trimethylnaphthalene and 1,2,5,6-tetramethylnaphthalene at elevated thermal maturities.

Whereas the distribution of trimethylnaphthalenes shows high variations for some isomers, the one of tetramethylnaphthalenes is dominated by fewer variations. 1,2,5,6-, 1,2,3,5-, 1,2,3,6- and 1,3,6,7-tetramethylnaphthalene are highly abundant for many samples. Due to the fact that the relative proportions 1,2,5-trimethylnaphthalene show strong correlation to the relative amounts of the coeluting compounds 1,2,5,6- and 1,2,3,5-tetramethylnaphthalene, it is presumed that the relative amounts of the two tetramethylnaphthalenes are strongly dominated by the relative proportions of 1,2,5,6-tetramethylnaphthalene. Although a natural source for 1,2,3,5-tetramethylnaphthalene has been suggested by Alexander *et al.* (1992), the authors did not suggest that 1,2,5-trimethylnaphthalene originates from the same source. Additionally a common source of the three compounds is unknown. In contrast a common source of 1,2,5-trimethylnaphthalene and 1,2,5,6-tetramethylnaphthalene has been suggested previously (Püttmann and Villar, 1987).

High concentrations of 1,3,6,7-tetramethylnaphthalene correspond to the enhanced thermal stability of this compound (van Duin *et al.*, 1997). It is present in high amounts in most of the samples at vitrinite reflectances beyond 0.65% R_r, but significantly increases for the few samples at maturity ranges above 1.08% R_r.

The high proportions of cadalene in most of the immature samples from the Viséan, give rise to the assumption, that this compound has been highly abundant in the flora of this region and period. Thermal instability of cadalene probably is the reason for its depletion in samples of later periods and higher thermal maturities.

6-Isopropyl-2-methyl-1(4-methylpentyl)naphthalene is present in many samples. Except for two samples, it is the only isomer present of the homologous series which Ellis *et al.* (1996) suggested to originate from resinous diterpenoids. It generally is a minor contributor to the group of alkylnaphthalenes.

Phenanthrene and Alkylphenanthrenes

Diterpenoids, showing an abietane and pimarane skeleton (Fig. 6.14) are likely biological precursors of alkylphenanthrenes (Simoneit *et al.*, 1986). These compounds are constituents of ambers and resins (Thomas, 1969; Simoneit *et al.*, 1986) present in vascular plants.

The most prominent alkylphenanthrene, directly attributed to diterpenoids of the abietane type is 1-methyl-7-isopropylphenanthrene (retene). 1,7-Dimethylphenanthrene (pimanthrene) probably originates from diterpenoids of the pimarane type (Fig. 6.14) but is also a potential decomposition product of retene (Simoneit *et al.*, 1986). Additionally phenanthrene and alkylphenanthrenes may originate from pentacyclic triterpenoids for example steroids (Streibl and Herout, 1969; Greiner *et al.*, 1976).

A detailed study on the distribution of alkylphenanthrenes regarding their potential biological origin and the dependence on maturity has been carried out by Budzinski *et al.* (1995). The authors compared distributions of methyl-, dimethyl- and trimethylphenanthrenes in samples originating from terrestrial and marine

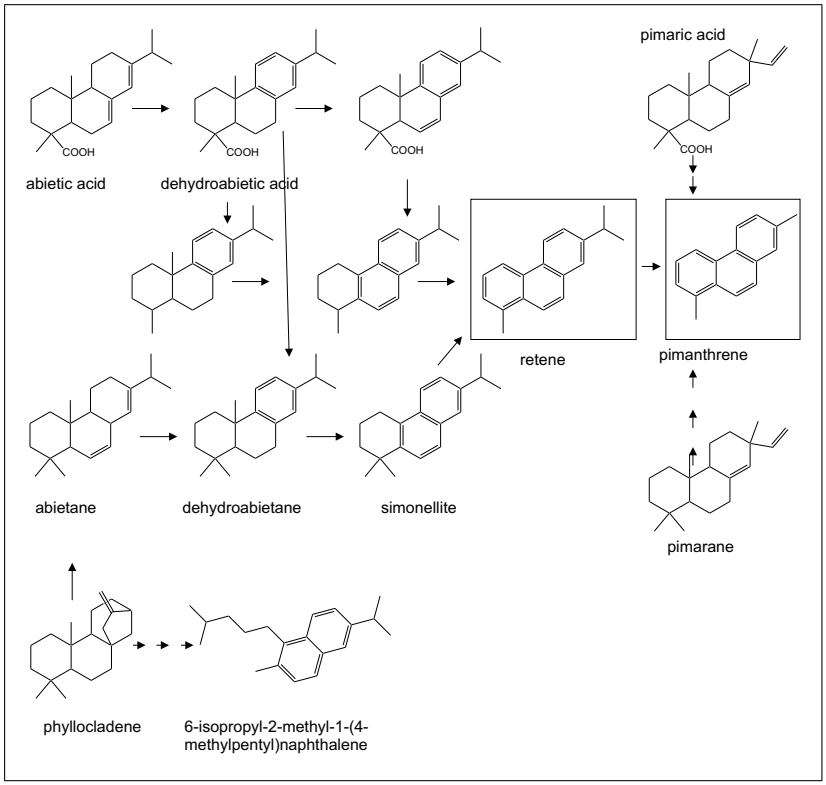

Figure 6.14: Possible pathways for the formation of retene and pimanthrene from diterpenoids after Simoneit (1986) and Alexander *et al.* (1987)

sources. High proportions of 1-methylphenanthrene were preferentially found in organic matter of terrestrial source rocks, whereas 9-methylphenanthrene was relatively enriched in organic matter from marine shales. Additionally a predominance of pimanthrene and retene has been attributed to terrestrial organic matter. Among trimethylphenanthrenes, 1,2,8-trimethylphenanthrene, in general was the most abundant isomer. The authors therefore suggested that it originates from an ubiquitous natural source.

While there is much evidence for the biological origin of alkylnaphthalenes, investigations on alkylphenanthrenes mainly address their common use as maturity parameters (Radke *et al.*, 1982b). In immature samples 9-methylphenanthrene and 1-methylphenanthrene often are highly abundant, with 9-methylphenanthrene being predominant (Radke *et al.*, 1982a). With increasing maturity 2-methylphenanthrene and 3-methylphenanthrene become more predominant, due

to their enhanced thermal stability. Normally 2-methylphenanthrene is present in higher proportions than 3-methylphenanthrene.

Based on these observations the Methylphenanthrene Ratios (MPI, Table 6.6) were established, showing excellent correlation with the vitrinite reflectance for organic material of type III kerogen (Radke *et al.*, 1982a). Therefore the vitrinite reflectance of terrestrial organic matter, with ratios of MPR <2.65 can be approximated by calculation (R_c, Table 6.6). MPI 2 normally is little enhanced in comparison to MPI 1, due to the slight predominance of 2-methylphenanthrene.

Relatively enhanced proportions of 2,6-, 2,3-, 2,7- and 3,6-dimethylphenanthrenes in a coal sample of high maturity, compared to a shale sample of lower maturity led to the suggestion, that these compounds are formed by isomerisation reactions of alkylphenanthrenes (Garrigues *et al.*, 1987). The enhanced stability of the β-substituted isomers at elevated maturity ranges is applied in the Dimethylphenanthrene Ratio (DPR, Table 6.6).Wilhelms *et al.* (1998) found an increase of the ratio of 3-methylphenanthrene/retene (Table 6.6) with increasing maturities.

Although high amounts of 9-methylphenanthrene have been attributed to indicate immature organic matter originating from marine sources, they may also result from a preferential methylation of alkylphenanthrenes at this position of the skeleton in the presence of acidic clay (Alexander *et al.*, 1995). Furthermore phenanthrenes showing a substitution at position 9 are supposed to be less susceptible to biodegradation (Bastow *et al.*, 1999).

In the samples studied in this project C_{0-2}-phenanthrenes (Fig. 6.15) and retene were identified according to literature. 1,2,8-Trimethylphenanthrene was identified by coelution with an authentic standard. Additionally 20 C_3- and 11 C_4-phenanthrenes have been quantified. The total amount of $C_{(0-4)}$-alkylphenanthrenes ranges between 71-2103 μg/g TOC (Table A.21). They are highly abundant in humic coals, but minor contributors to the samples characterised by low proportions of vitrinite and inertinite. However, the relative amounts of alkylphenanthrenes do not correlate to vitrinite reflectances, inertinite or vitrinite proportions.

Table 6.6: Maturity parameters based on the relative abundance of different alkylphenanthrenes

Name	Formula	Reference
MPI 1	$\frac{1.5(2-MP+3-MP)}{P+1-MP+9-MP}$	Radke *et al.* (1982a)
MPI 2	$\frac{3(2-MP)}{P+1-MP+9-MP}$	Radke *et al.* (1982a)
R_c	0.60 MPI 1 + 0.40 (for MPR <2.65)	Radke *et al.* (1986)
MPR	$\frac{2-Methylphenanthrene}{1-Methylphenanthrene}$	Radke *et al.* (1982b)
MPR 1	$\frac{1-Methylphenanthrene}{Phenanthrene}$	Radke *et al.* (1982a)
MPR 2	$\frac{2-Methylphenanthrene}{Phenanthrene}$	Radke *et al.* (1982a)
MPR 3	$\frac{3-Methylphenanthrene}{Phenanthrene}$	Radke *et al.* (1982a)
MPR 9	$\frac{9-Methylphenanthrene}{Phenanthrene}$	Radke *et al.* (1982a)
DPR	$\frac{2,6-+2,7-+3,5-DMP}{1,3-+1,6-+2,5-+2,9-+2,10-+3,9+3,10-DMP}$	Radke *et al.* (1986)
3-MP/Retene	$\frac{3-Methylphenanthrene}{Retene}$	Wilhelms *et al.* (1998)

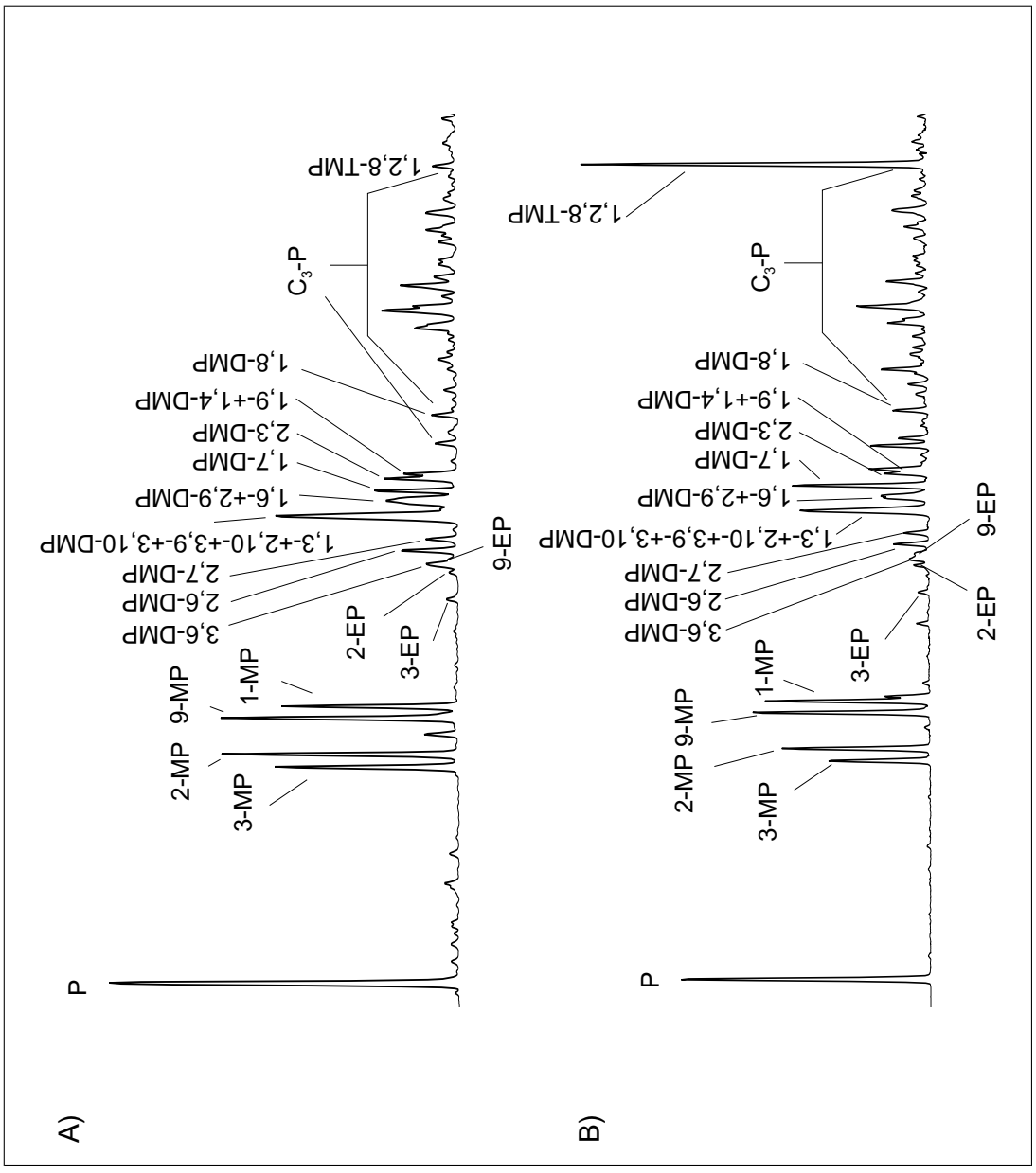

Figure 6.15: Gas Chromatogram (m/z 178, 192, 206, 220, 234) of alkylphenanthrenes in A) an Upper Carboniferous and B) a Permian sample

The calculated vitrinite reflectances R_c (Fig. 6.16) normally are in good agreement with the measured vitrinite reflectances of the samples. Strong deviations are restricted to the samples predominantly containing type I kerogen or showing relatively high proportions of minerals.

Whereas the calculated vitrinite reflectances show higher values for the immature samples which are determined by high proportions of type I kerogen organic matter, they show lower values for samples characterised by high proportions of minerals. It is probable that the inorganic matrix influences the thermal behaviour of the organic matter or that the minerals support methyl shift reactions leading to an increase of 9-methylphenanthrene. Most of the samples that show strong deviations are characterised by high proportions of phenanthrene. Normally either 2- or 9-methylphenanthrene are the predominant methylphenanthrenes. With one exception, 2-methylphenanthrene is present in higher amounts than 3-methylphenanthrene. Further ratios, like the DPR (Fig. 6.16) are also in good correlation with the vitrinite reflectances for most of the samples. This does not account for samples of low maturities and a predominance of type I kerogen. The ratio of 3-methylphenanthrene to retene shows no correlation to vitrinite reflectances.

1,7-Dimethylphenanthrene (pimanthrene) compared to other dimethylphenanthrenes is relatively enriched. The ratio of retene to pimanthrene varies widely in the range of 0.0-5.7. It is significantly high for some immature samples of the Viséan, but also for few samples of the Upper Carboniferous and the *Sigillaria*. The relative high proportions of retene in immature samples is due to the low thermal stability of this compound in comparison to pimanthrene. A relative decrease of pimanthrene at elevated maturities probably results from the destruction of retene. Nevertheless the relative high concentrations of retene in for example the *Sigillaria* shows that different biological precursors of the two compounds may also influence their relative amounts.

Besides pimanthrene the distribution of dimethylphenanthrenes and ethylphenanthrenes does not differ significantly. Variations seem to be mainly influenced by the maturity of the samples. This is due to the fact, that the DPR, i.e. the distribution of dimethylphenanthrenes showed good correlation to the vit-

rinite reflectances of the samples (Fig. 6.16). A relative enrichment of 1,9- and 4,9-dimethylphenanthrene for samples, that show enhanced proportions of 9-methylphenanthrene indicates a relationship between the compounds. 3,6-Dimethylphenanthrene is present in relatively high concentrations in some samples that show no high thermal maturity. High proportions of this compound have been attributed to samples of enhanced maturities (Budzinski *et al.*, 1995) while a potential biogenic precursor is unknown.

C_3-Phenanthrenes and C_4-phenanthrenes are normally present in lower amounts than their lower homologues. This does not account for retene. Additionally the relative amounts of 1,2,8-trimethylphenanthrene vary widely.

Anthracene and 2- and 1-methylanthracene due to their molecular structure are related to alkylphenanthrenes. In comparison to alkylphenanthrenes they are characterised by depleted thermal stabilities. Therefore they normally are minor

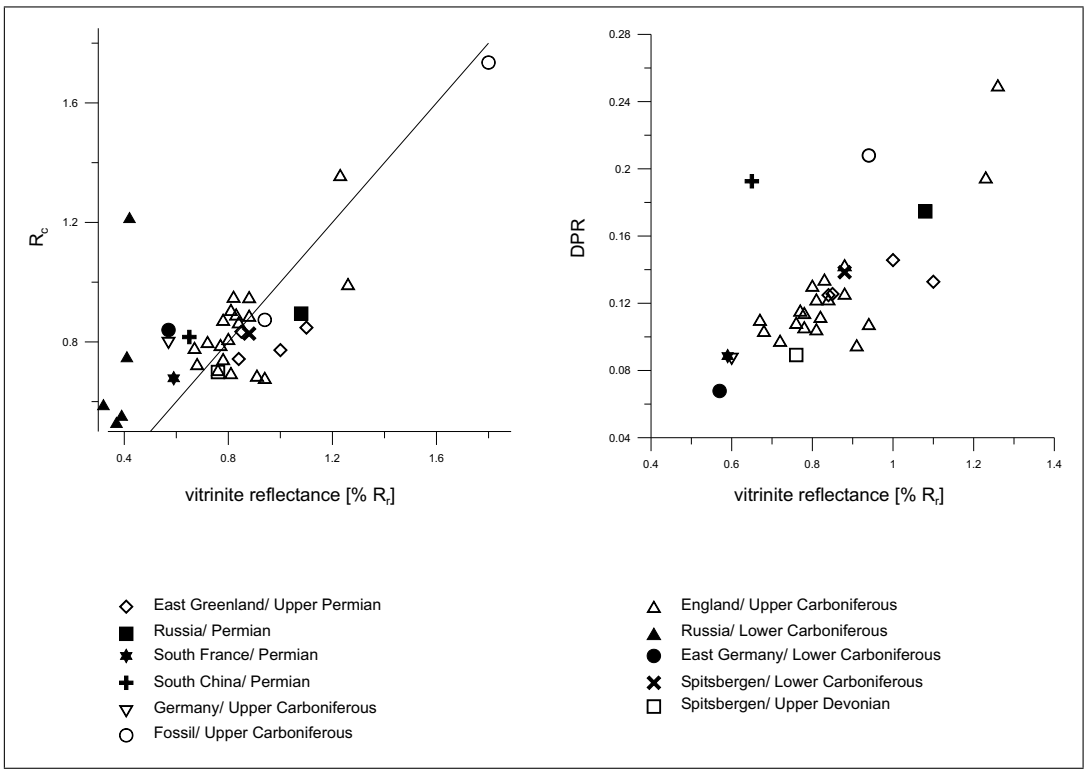

Figure 6.16: Cross plot of A) vitrinite reflectance *vs.* MPI-1 (R_c) and B) vitrinite reflectance *vs.* DPR

contributors to the fraction of aromatic hydrocarbons. They were only present in significant amounts in the two samples originating from Germany.

Biphenyl and Alkylbiphenyls

Alkylbiphenyls often are major contributors to the aromatic fractions of petroleum and petroleum source rocks, but have also been found in coal extracts (Alexander *et al.*, 1986a). Their biological origin is uncertain. The compounds are present in organic matter originating from different geological ages and different source types. Their occurrence can be dated back to the Middle Cambrian, a period that predates the evolution of higher plants (Cumbers *et al.*, 1987).

Biphenyl and alkylbiphenyls are combustion products of benzene and alkylbenzenes (Takatsu and Yamamoto, 1993). Kruge *et al.* (1994) found high proportions of biphenyl in samples that showed high concentrations of semifusinite and pyrofusinite. Semifusinite and pyrofusinite result from the partial combustion of organic matter. Alexander *et al.* (1994) showed that the relative abundances of alkylcyclobenzenes and alkylbiphenyls in crude oils are of the same magnitude. The authors therefore suggest, that these compounds are formed via deposition of oxygen-rich source materials in oxic depositional environments. Alkylcyclohexylbenzenes and alkylbiphenyls may be products of the oxidative coupling of phenols (Alexander *et al.*, 1994).

Besides the little knowledge on direct biological precursors of alkylbiphenyls their potential as maturity indicators is also sparse. *Para*- and *meta*-substituted alkylbiphenyls, i.e. 4- and 3-alkylbiphenyls are more stable, than 2-alkylbiphenyls. A depletion of *ortho*-substituted alkylbiphenyls therefore is observed in samples of enhanced maturities. The depletion probably results from either isomerisation reactions (Cumbers *et al.*, 1987) or cyclisation reactions (Kagi *et al.*, 1990). The latter reactions are supposed to involve free radicals and to result in the formation of alkylfluorenes (Kagi *et al.*, 1990). To some extent alkylbiphenyls may serve as maturity indicators. A relative increase in the ratio of 3-methylbiphenyl/2-methylbiphenyl may indicate an enhanced maturity of the organic matter. However the ratio is suggested to depend on the kerogen type (Alexander *et al.*,

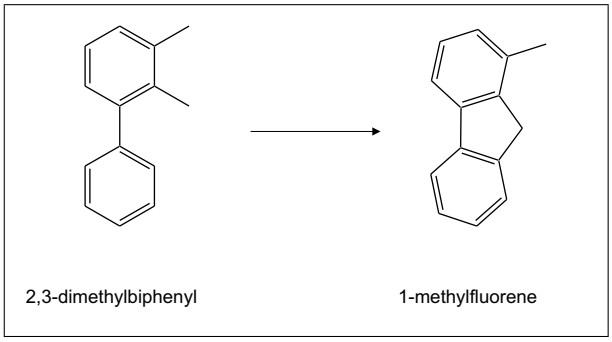

Figure 6.17: Heating experiments carried out by Alexander *et al.* (1988) showed that 1-methylfluorene is a cyclisation product of 2,3-dimethylbiphenyl

1986a). Investigations on the susceptibility towards biodegradation showed that para-substituted isomers are less degradable, whereas biphenyl is degraded first (Trolio *et al.*, 1999).

Alkylbiphenyls with up to C_5-substituents were present as minor compounds in most of the samples. Due to their low concentrations and their coelution with alkylnaphthalenes only biphenyl, C_1- and few C_2-biphenyls were quantified.

The amounts of alkylbiphenyls range from 1 to 211 μg/g TOC (Table A.23). The relative proportions of different isomers do not vary significantly. Except for one sample 3-methylbiphenyl is the most abundant compound. The distribution of methylbiphenyls shows no dependence on the maturity of the samples, either.

Alkylbiphenyls normally are of low abundance in the immature samples, that additionally were not deposited under oxic conditions. However, no correlation between the proportion of alkylbiphenyls and the depositional environment for example the ratio of pristane/phytane was found.

Fluorene and Alkylfluorenes

Fluorene and alkylfluorenes, in correspondence to biphenyl and alkylbiphenyls are ubiquitous compounds in sediments (Mojelsky and Strausz, 1986). They have often been reported to result from pyrolysis or incomplete combustion of diverse organic materials (Mojelsky and Strausz, 1986). As mentioned previously, Kagi *et al.* (1990) suggested, that alkylfluorenes yield from cyclisation reactions of *ortho*-substituted biphenyls. Indeed Alexander *et al.* (1988) showed that 2,3-

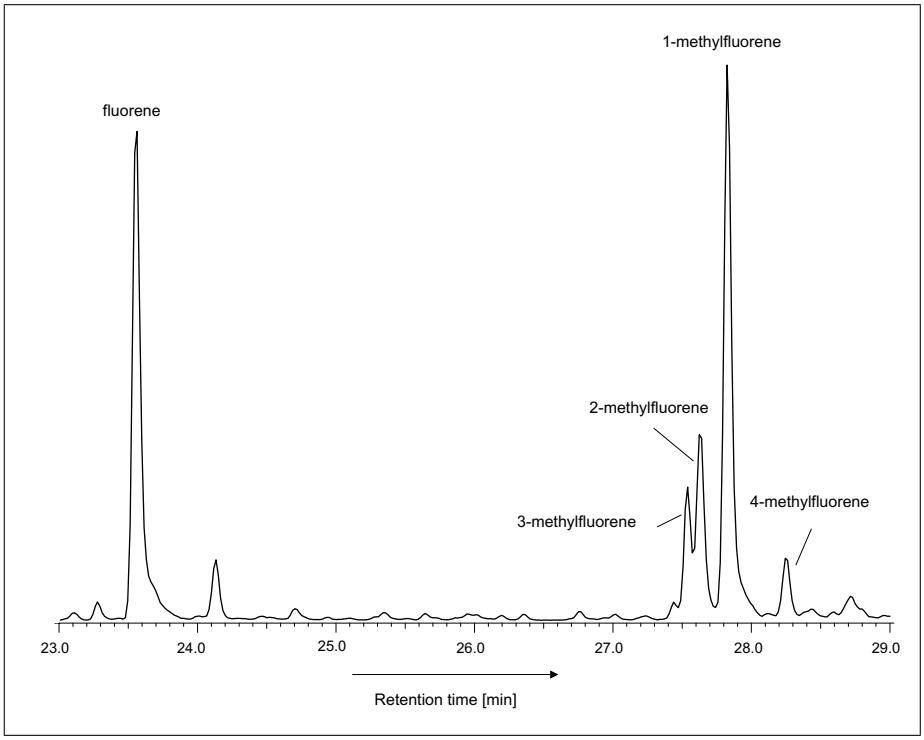

Figure 6.18: Gas Chromatogram of fluorene and methylfluorenes (m/z 166, 180) in an Upper Carboniferous sample

dimethylbiphenyl is transformed to 1-methylfluorene in heating experiments (Fig. 6.17). Nevertheless in sediments no direct correlation between the decrease of 2,3-dimethylbiphenyl and the increase of 1-methylfluorene has been found (Alexander *et al.*, 1988). The authors suggested, that the depletion of 2,3-dimethylbiphenyl does not depend on matrix effects, but on the maturity of the sediments.

Fluorene and alkylfluorenes are only minor contributors to the aromatic fraction. Fluorene and methylfluorenes were quantified for all samples, except one. Amounts of the summed five compounds range from 0.1 to 107.4 μg/g TOC (Table A.24). They show enhanced proportions in the more mature samples and are relatively depleted in samples of low maturities. Fluorene is generally present in lower amounts than its alkylated homologues. The distribution of methylfluorenes shows no significant variations for different samples. In general 1-methylfluorene is the most abundant methylfluorene, whereas 4-methylfluorene is by far the least abundant (Fig. 6.18). 2- and 3-Methylfluorene are normally present in equal amounts (Fig. 6.18).

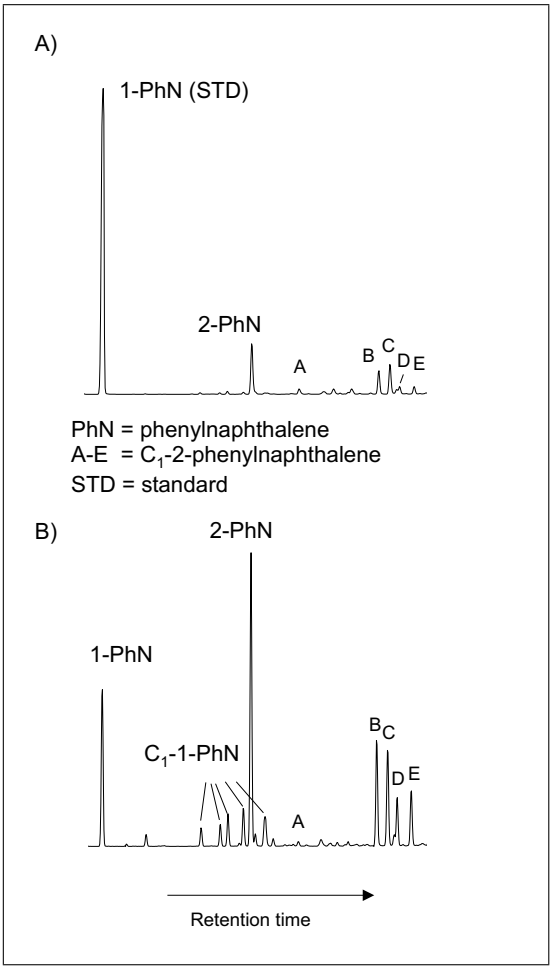

Figure 6.19: Gas Chromatogram of C_{0-1}-phenylnaphthalenes (m/z 204, 218) in A) a coal from the Upper Carboniferous, where 1-phenylnaphthalene has been added as a standard and B) a sediment from the Permian where 1-phenylnaphthalene has not been added as a standard

Phenylnaphthalenes and Alkylphenylnaphthalenes

Phenylnaphthalenes and alkylphenylnaphthalenes are known to be constituents of fossil organic matter (White and Lee, 1980). However, they were no subject to intensive investigations in organic geochemistry. This may be due, to the lack of any obvious biogenic precursors. Like fluorene and alkylfluorenes they have been reported as pyrolysis products of organic matter (Meyer zu Reckendorf, 1997). It is assumable, that phenylnaphthalenes and their higher homologues, in correspondence to phenyldibenzofurans are products of radical phenylation (Meyer zu Reckendorf, 1997).

More detailed investigations on phenylnaphthalenes have been carried out by Marynowski *et al.* (2001). The authors found that the relative amounts of 1-

and 2-phenylnaphthalene depend on maturity. Due to its enhanced thermal stability, 2-phenylnaphthalene has been found to be relatively enriched at enhanced maturity ranges.

Phenylnaphthalenes and alkylnaphthalenes were present in almost all of the samples (Fig. 6.19). The amounts of 1-phenylnaphthalene, the earlier eluting phenylnaphthalene, could not be determined, due to the compound being added as a standard prior to extraction for most of the samples. Alkyl-1-phenylnaphthalene isomers, in analogy are supposed to elute earlier than the corresponding alkyl-2-phenylnaphthalenes (pers. comm. H. Willsch, FZ-Jüelich). Normally methyl-1-phenylnaphthalenes were minor contributors in comparison to methyl-2-phenylnaphthalenes (Fig. 6.19 A). Compounds based on the 1-phenylnaphthalene skeleton have generally not been quantified. Total total amounts of summed 2-phenylnaphthalene and five methyl-2-phenylnaphthalenes range from 2.8 to 290 μg/g TOC (Table A.25). They are normally enriched in samples of enhanced maturities and depleted in samples of low maturities that have not been deposited under oxic conditions. In general the relative concentrations are comparable to those of alkylbiphenyls and alkylfluorenes. The distribution of alkylphenylnaphthalenes does not differ significantly for different samples. Normally 2-phenylnaphthalene is significantly enriched compared to its methylated homologues. This does not account for few samples of low maturities.

Resumée

Alkylynaphthalenes and alkylphenanthrenes, were present in all of the investigated samples. Alkylbiphenyls, alkylfluorenes and alkylphenylnaphthalenes have been quantified in all samples except one. Anthracene and 1- and 2-methylanthracene in quantifiable amounts have only been present in two samples.

Generally aromatic compound classes are present in higher amounts in samples of maturities beyond 0.6% R_r. With few exceptions the sum of quantified alkylphenanthrenes is higher than the sum of quantified alkylnaphthalenes. Alkylbiphenyls, -fluorenes and -phenylnaphthalenes are minor contributors to the fractions of aromatic hydrocarbons. Alkylfluorenes are less abundant in samples of the

Viséan exhibiting low maturities, while $C_{(0-1)}$-2-phenylnaphthalenes are relatively enriched in these samples.

Whereas the distribution of alkylybiphenyls, alkylfluorenes and alkylphenylnaphthalenes showed little variations, this does not account for alkylnaphthalenes and alkylphenanthrenes. Distribution of alkylnaphthalenes was characterised by a slight dependence on the maturity, only (Fig. 6.13, Table 6.5). Few isomers like 1,3,6,7-tetramethylnaphthalene show high proportions, attributed to their enhanced thermal stability at elevated maturities. Cadalene, a higher plant biomarker has been highly abundant in samples of the Viséan, characterised by low maturities. 1,2,5-Trimethylnaphthalene and 1,2,5,6-tetramethylnaphthalene often are highly abundant. This does also account for 1,6-dimethylnaphthalene. These three alkylnaphthalenes, in contrast to their depleted thermal stability show weak correlation to vitrinite reflectance. 6-Isopropyl-2-methyl-1-(4-methylpentyl)-naphthalene, was the only isomer of a homologuous series present. The compound and its lower isomers were suggested to originate from resinous diterpenoids. However, concentrations of 6-isopropyl-2-methyl-1-(4-methylpentyl)naphthalene were generally low.

In contrast to alkylnaphthalenes maturity ratios based on the relative amounts of different alkylphenanthrenes, for example the MPI and the DPR are in good correlation to vitrinite reflectances (Fig. 6.16). Retene and pimanthrene are often highly abundant. Their relative proportions, contrary to cadalene show no dependence on the maturity. A difference in origin for the two compounds is suggested.

None of the potential biomarkers cadalene, retene and pimanthrene have been absent in a time period. 1,2,7-Trimethylnaphthalene is characterised by elevated proportions for immature samples and the high proportions of 1,2,8-trimethylphenanthrene in many samples indicate that there is a specific biogenic source for this compound.

6.4 NSO Compounds

Introduction

NSO compounds incorporate nitrogen (N), sulphur (S) and/or oxygen (O) atoms. These hetero-atoms are present either in so-called hetero-cycles, which often show an aromatic skeleton (carbazoles, dibenzothiophenes, dibenzofurans) or in peripheral functional groups. Oxygen is the most prominent hetero-atom present in functional groups such as ketones, aldehydes, alcohols and phenols or carboxylic acids.

Even though the finding of nitrogen-containing compounds (porphyrins) in the 1930s often is regarded to be the beginning of modern organic geochemistry, investigations on NSO compounds in fossil organic matter are rare in comparison to those on aliphatic and aromatic hydrocarbons. In fact, for a long period nitrogen containing tetrapyrrolye pigments have received more attention than other NSO compound types (Baker and Louda, 1986). However, it is presumable that the more complex skeleton of polar constituents may contain even more information about biogenic relationships than their aromatic and aliphatic counterparts.

6.4.1 Low-Polarity NSO Compounds

Introduction

Besides the compounds like alkyldibenzofurans and -dibenzothiophenes, which incorporate a hetero-atom in the aromatic or aliphatic ring system, ketones and aldehydes are also constituents of the low-polarity NSO compound fraction. The former two compound classes due to their low polarity were constituents of the aromatic hydrocarbon fraction. In the investigated compound classes sulphur and nitrogen were only present in aromatic hetero-cycles, i.e. dibenzothiophenes and carbazoles. In contrast oxygen containing compounds in the low-polarity NSO compound fraction differ more widely, with dibenzofurans, dibenzo[*b*]naphthofurans,

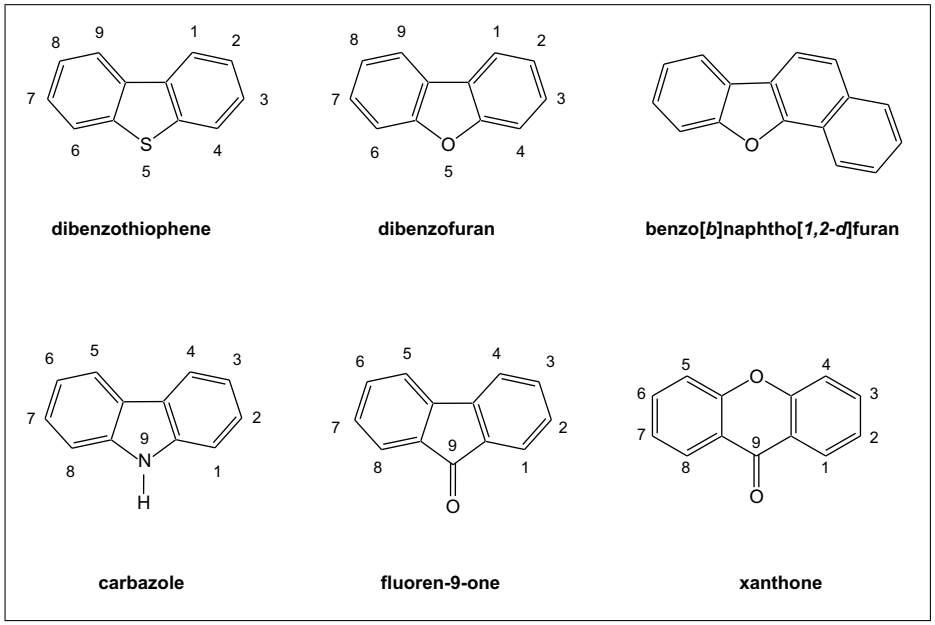

Figure 6.20: Different tricyclic- and tetracyclic aromatic NSO compounds and their ring numbering conventions

fluoren-9-ones, xanthones, naphthaldehydes and acetylnaphthalenes being present.

Dibenzothiophene and Alkyldibenzothiophenes

A specific biological source of dibenzothiophene and alkyldibenzothiophenes is unknown. Indeed it is generally accepted that the major part of the organically-bound sulphur is generated in sediments randomly (Arpino *et al.*, 1987; Sinninghe Damsté and de Leeuw, 1990). It has been suggested that alkyldibenzothiophenes are formed via reactions of biomolecules with reduced sulphur (Fig. 6.21), i.e. hydrogen sulphide and polysulphides under anoxic conditions and low concentrations of iron (Orr and Sinninghe Damsté, 1990; Hughes *et al.*, 1995). Therefore the formation of alkyldibenzothiophenes is supposed to be controlled by environmental factors, i.e. the availability of reduced sulphur in sediments. The availability of reduced sulphur in turn is related to the activity of sulphate-reducing bacteria and limited by the availability of sulphate as an electron acceptor for microbial oxidation of organic matter.

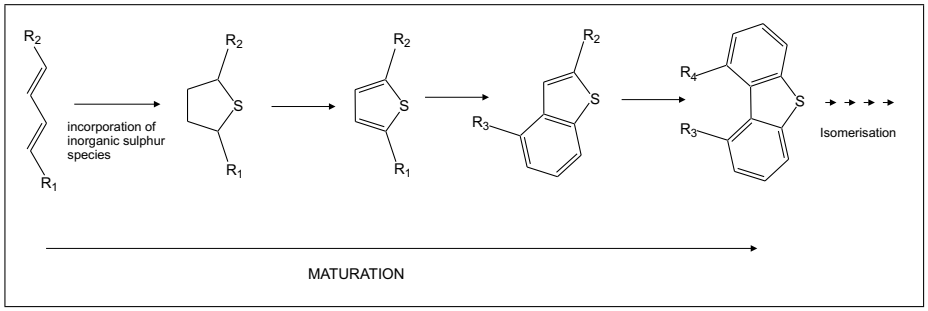

Figure 6.21: Possible diagenetic formation of alkyldibenzothiophenes after Sinninghe Damsté and de Leeuw (1990)

Table 6.7: Maturity parameters based on the relative proportions of different alkyldibenzothiophenes

Name	Formula	Reference
MDR	$\frac{4-MDBT}{1-MDBT}$	Radke *et al.* (1986)
MDR´	$\frac{4-MDBT}{1-MDBT+4-MDBT}$	Radke and Willsch (1994)
EDR´	$\frac{4,6-DMDBT}{4-EDBT+4,6-DMDBT}$	Radke and Willsch (1994)

High proportions of dibenzothiophene and alkyldibenzothiophenes are characteristic for marine shales and carbonates, whereas their presence in continental facies is generally low (Radke *et al.*, 1991). This relationship between alkyldibenzothiophene concentrations and organic facies is expressed in the ratio of dibenzothiophene to phenanthrene (Radke *et al.*, 1991; Hughes *et al.*, 1995). Ratios of dibenzothiophene to phenanthrene in the range of 0.06-0.2 are typical for coals, i.e. terrestrial organic matter (Requejo, 1994).

The relative proportions of individual alkyldibenzothiophenes in contrast are suggested to depend on the maturity of organic matter. A relative increase of 4-methyldibenzothiophene during maturation is attributed to its higher thermal stability (Radke *et al.*, 1986). The Methyldibenzothiophene Ratios (MDR and MDR´ , Table 6.7) base on a decrease of 1-methyldibenzothiophene with increasing maturity, accompanied by an increase of 4-methyldibenzothiophene. Dzou

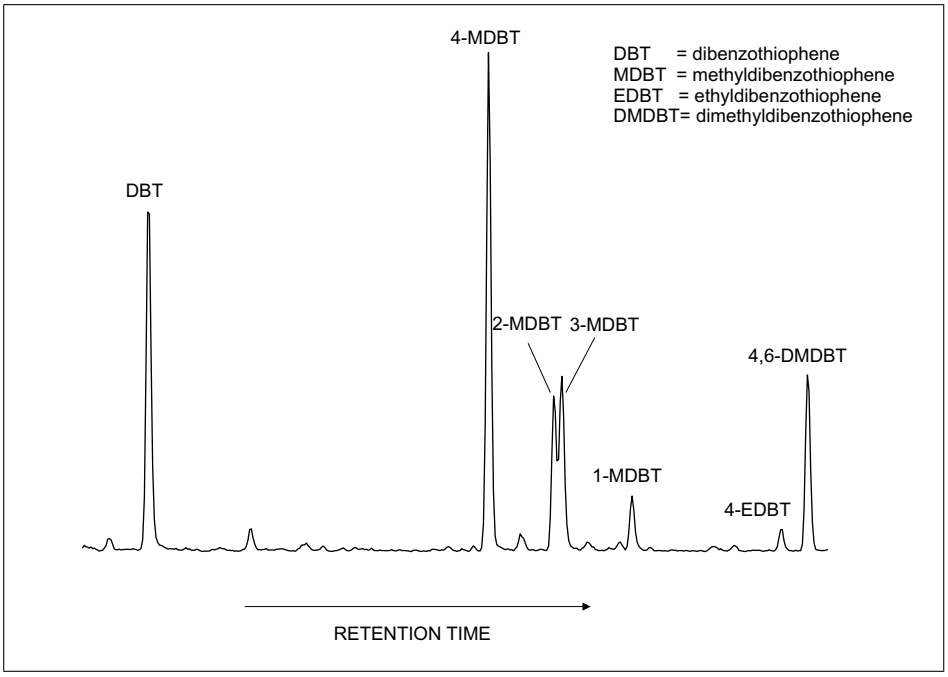

Figure 6.22: Gas Chromatogram of alkyldibenzothiophenes (m/z 184, 198, 212) of an Lower Carboniferous coal

et al. (1995) for a set of Carboniferous coals and vitrinite concentrates found a constant amount of 1-methyldibenzothiophene within wide maturity ranges, and an increase of 4-methyldibenzothiophene with increasing maturity. The authors therefore suggested that isomerisation reactions play a minor role in controlling the distribution of methyldibenzothiophenes. In contrast Chakhmakhchev *et al.* (1997) for a set of oil and condensate samples from various geological periods found no dependence of the MDR on the vitrinite reflectances. An influence of depositional environment and lithology on the distribution of alkyldibenzothiophenes below maturities of 1.35% R_r, especially for coals may account for these observations (Radke *et al.*, 2000; Dzou *et al.*, 1995). The EthylDibenzothiophene Ratio (EDR´) has also been applied to estimate the maturity of organic matter. It considers the relative increase of 4,6-dimethyldibenzothiophene in comparison to 4-ethyldibenzothiophene (Table 6.7).

In the samples studied in this project, dibenzothiophene, methyldibenzothiophenes, 4-ethyldibenzothiophene and 4,6-dimethyldibenzothiophene (Fig. 6.22) have been identified according to their mass spectra and to literature. Further

alkyldibenzothiophenes have not been assigned, due to the generally low abundance of this compound class. The relative amounts of the summed isomers are in the range of 0-100 μg/g TOC (Table A.29). Alkyldibenzothiophenes were absent in few samples, only (Table A.29). They are highly abundant in samples of enhanced maturities, but also in some characterised by low maturity but high TS-contents (Table A.1).

At vitrinite reflectances beyond 0.6% R_r distributions of methyldibenzothiophenes for many samples are in good correlation with maturities (Fig. 6.23A). However this does not account for samples of low maturities (Fig. 6.23 A), showing elevated proportions of 4-methyldibenzothiophene. Additionally some samples, predominantly characterised by high proportions of minerals show relatively enhanced proportions of 1-methyldibenzothiophene and therefore no good correlation between MDR´ and vitrinite reflectance (Fig. 6.23 A). This in contrast is not observed for the EDR´ . Although a slight correspondence between maturity and EDR´ for maturities beyond 0.5% R_r can be suggested, variations are wide (Fig. 6.23B).

The high proportions of 4-methyldibenzothiophene for the immature samples correspond to elevated proportions of 4,6-dimethyldibenzothiophene. This supporting the hypothesis that the MDR and therefore also the MDR´ do not exclusively depend on the maturity of the organic matter but on the type of organic matter (Orr and Sinninghe Damsté, 1990).

The low amounts of dibenzothiophene in comparison to the amounts of phenanthrene (Fig. 6.24), for the majority of the samples, in correspondence to Hughes *et al.* (1995) indicate, that organic matter has predominantly been deposited in lacustrine or fluvio/deltaic environments. It should be noticed that this classification due to the low amounts of alkyldibenzothiophenes is determined by the ratio of pristane/phytane only. Due to the low amounts of alkyldibenzothiophenes in this study, the significance of alkyldibenzothiophene composition and concentrations therefore should not be overestimated. Nevertheless the low amounts indicate, that the conditions have not been ideal for the formation of alkyldibenzothiophenes.

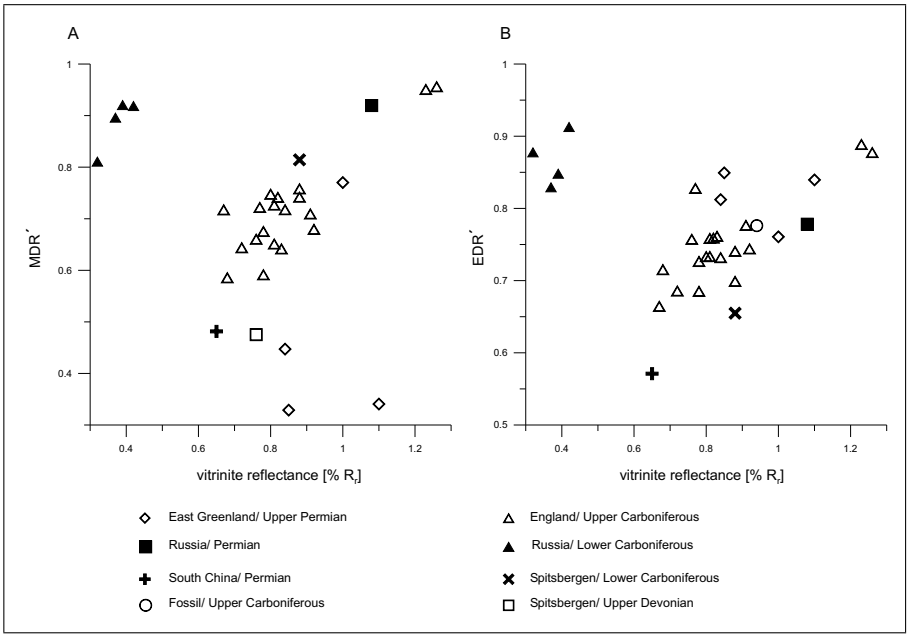

Figure 6.23: Cross plot of A) MDR´ and B) EDR´ *vs.* vitrinite reflectance

Zone	DBT/P	pristane/phytane	Depositional Environment	Lithology
1A	>3	<1	Marine	Carbonate
1B	1-3	<1	Marine and Lacustrine	Carbonate and mixed
2	<1	<1	Lacustrine (sulphate-poor)	Variable
3	<1	1-3	Marine and Lacustrine	Shale
4	<1	>3	Fluvio/Deltaic	Carbonaceous Shale and Coal

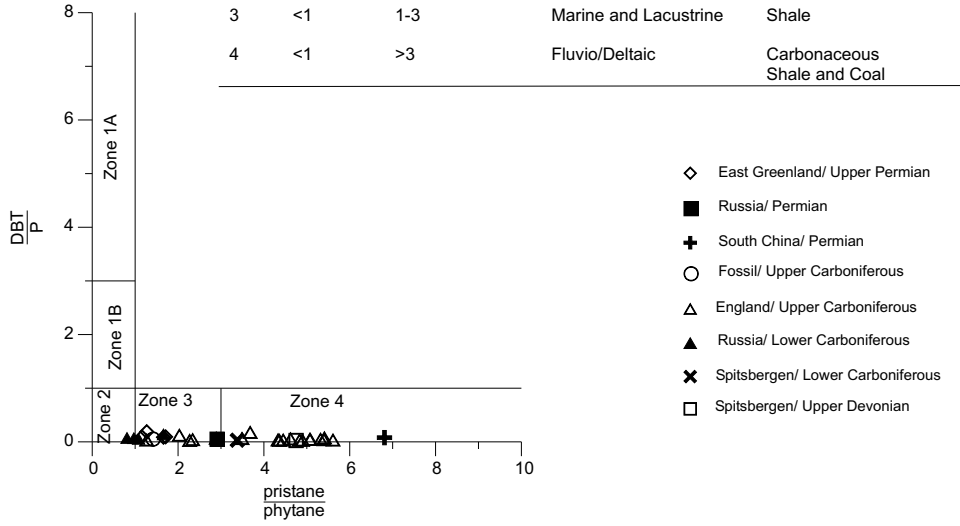

Figure 6.24: Cross plot of dibenzothiophene/phenanthrene (DBT/P) *vs.* pristane/phytane

Dibenzofuran and Alkyldibenzofurans

A systematic investigation on the occurrence and distribution of dibenzofuran and alkyldibenzofurans has only been carried out few years ago by Radke *et al.* (2000). However the presence of these compounds in bituminous coals has already been recognised by Hayatsu *et al.* (1978b). Those findings correspond to the observations of Radke *et al.* (2000), that these compounds preferentially are released at vitrinite reflectances of around 0.77% R_r. In comparison to alkyldibenzothiophenes, alkyldibenzofurans are enriched in organic matter originating from terrigenous sources. Their predominance is attributed to the deposition of higher plant debris in lacustrine environments (Radke *et al.*, 2000; Sephton *et al.*, 1999). The ratios of dibenzofuran to dibenzothiophene and methyldibenzofurans to methyldibenzothiophenes therefore, in correspondence to the ratios of Hughes *et al.* (1995) have been applied to obtain information on the facies of the organic matter (Kruge, 2000; Radke *et al.*, 2000).

A direct biological precursor of alkyldibenzofurans is unknown. It has been suggested, that tannins, showing a polycondensed phenolic structure may be biological precursors. Another assumption points out, that alkyldibenzofurans may originate from condensed and dehydrated polysaccharides (Sephton *et al.*, 1999) via thermally controlled aldol, retro-aldol or Diels-Alder reactions. Additionally dibenzofuran metabolites (Fig. 6.25), substituted at different positions of the dibenzofuran skeleton are constituents of lichens. It has been suggested that variations in concentrations of 1-methyldibenzofuran correspond to secondary metabolism of dibenzofuran metabolites present in lichens (Radke *et al.*, 2000). Although little is known about the recognition of lichens in the Paleozoic it has been suggested, that environments, where conifers or their primitive precursors are abundant could also be good habitats for lichens. Additionally the evolution of lichens can be dated back to the Early Devonian (Taylor *et al.*, 1995).

The biogenic relationship corresponds to a predominance of 1-methyldibenzofuran in samples of elevated maturities. The findings indicate, that 1-methyldibenzofuran, the least stable of the four methyldibenzofurans is produced kinetically (Radke *et al.*, 2000). However high amounts of 1-methyldibenzofuran

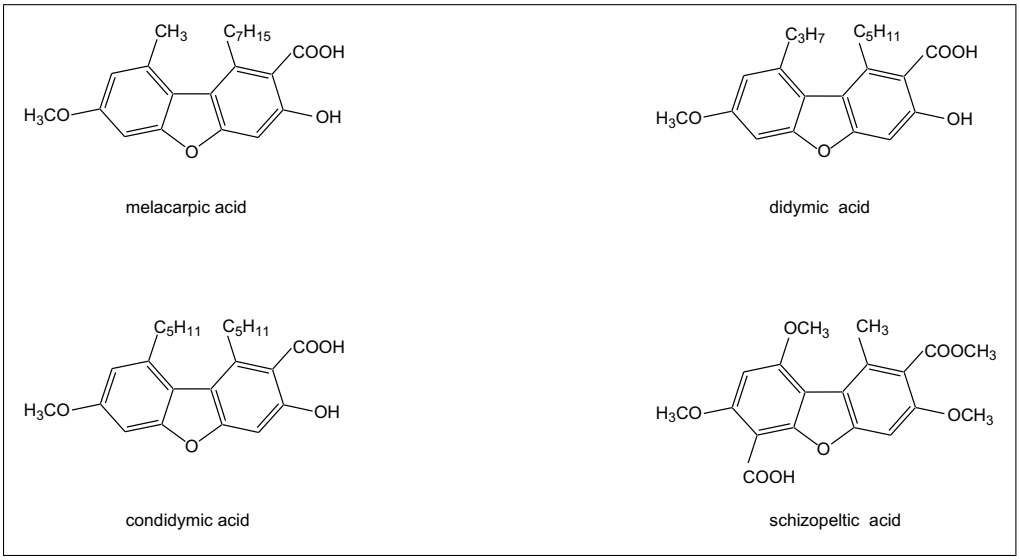

Figure 6.25: Dibenzofuran metabolites present in extant lichens

may also result from free radical methylation. Radke *et al.* (2000) suggested, that in analogy to the preferential formation of 9-methylphenanthrene via free radical methylation this could also account for 1-methyldibenzofuran.

Dibenzofuran and methyldibenzofurans in this study were assigned by mass spectra and literature (Radke *et al.*, 2000). Besides, eleven peaks attributed to C_2-dibenzofurans were identified (Fig. 6.26). Among the C_2-dibenzofurans, two isomers (No.2 and No.7) are inferred to be ethyldibenzofurans. Their mass spectra show a base peak at m/z 181 (M^+-CH_3). The high proportions of peak No.8 probably can be attributed to a coelution of different dimethyldibenzofurans.

Summed amounts of $C_{(0-2)}$-dibenzofurans range from 10 to 1930 μg/g TOC (Table A.31). Samples showing low maturities often are characterised by elevated proportions of dibenzofuran. Among the methyldibenzofurans, 4-methyldibenzofuran and 2-methyldibenzofuran often are the most abundant isomers. With increasing maturity a relative increase of 1-methyldibenzofuran is observed (Fig. 6.27). However the ratio of 1-methyldibenzofuran/(1- and 4-methyldibenzofuran) does not correspond to maturity unambiguously (Fig. 6.27). Samples characterised by elevated amounts of minerals often show high proportions of 1-methyldibenzofuran.

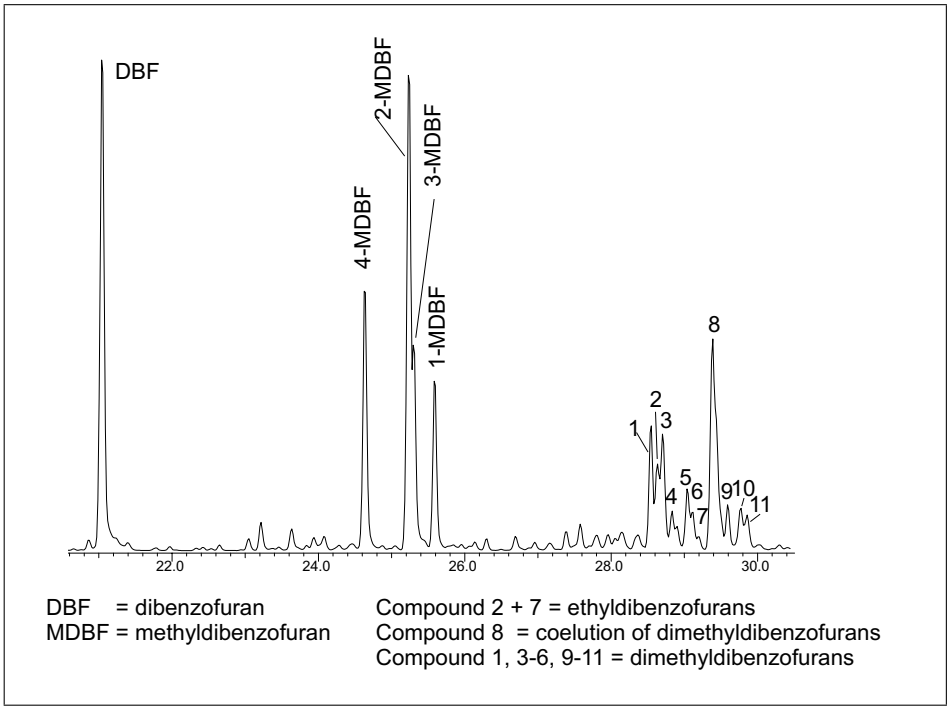

Figure 6.26: Gas Chromatogram of C_{0-2}-dibenzofurans (m/z 168, 182, 196) of an Upper Carboniferous sample

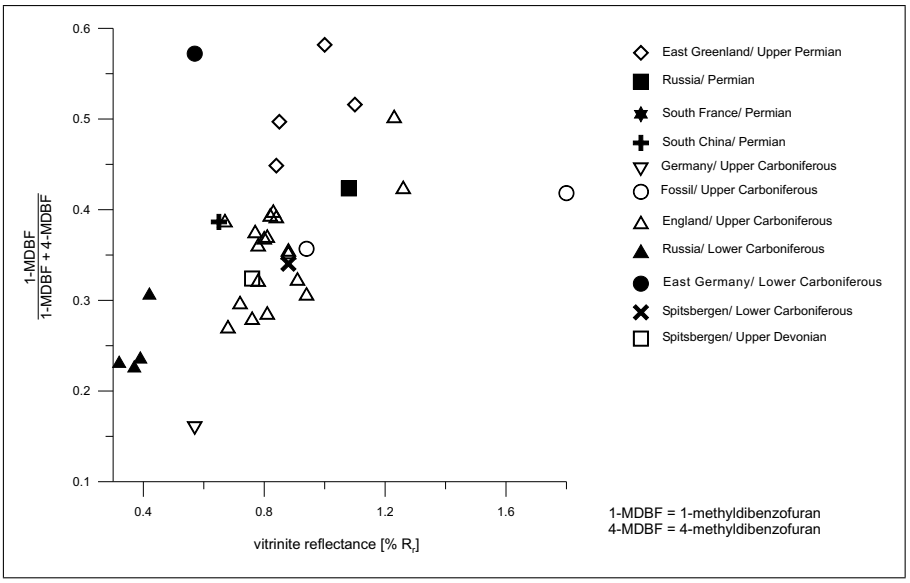

Figure 6.27: Cross plot displaying the ratio of 1-methyldibenzofuran/(1-methyldibenzofuran + 4-methyldibenzofuran) *vs.* vitrinite reflectance

In general the distribution of C_2-dibenzofurans shows less significant variations. Normally the first eluting C_2-dibenzofurans are present in higher proportions (Fig.

6.26). In correspondence to methyldibenzofurans, few isomers of dimethyldibenzofuran however show a slight correlation with vitrinite reflectance. For samples of vitrinite reflectances higher than 0.57% R_r an increase of dimethyldibenzofuran No. 5 is accompanied by a decrease of dimethyldibenzofuran No. 11 (Fig. 6.28). Additionally the two ethyldibenzofurans are absent in some samples of low but also in some of elevated maturity.

In analogy to Hughes *et al.* (1995), the relative amounts of alkyldibenzofurans to alkyldibenzothiophenes serve to determine the depositional environment and the lithology of organic matter (Radke *et al.*, 2000). Due to the elevated ratio of pristane/phytane for the majority of the samples, the cross plot is of little significance, indicating fluvio/deltaic depositional conditions. However for samples of depleted pristane/phytane ratios the plot may be more detailed than the one of Hughes *et al.* (1995). It is indicated that some samples with pristane/phytane ratios higher than one, may additionally be composed of marine derived organic matter (Fig. 6.29).

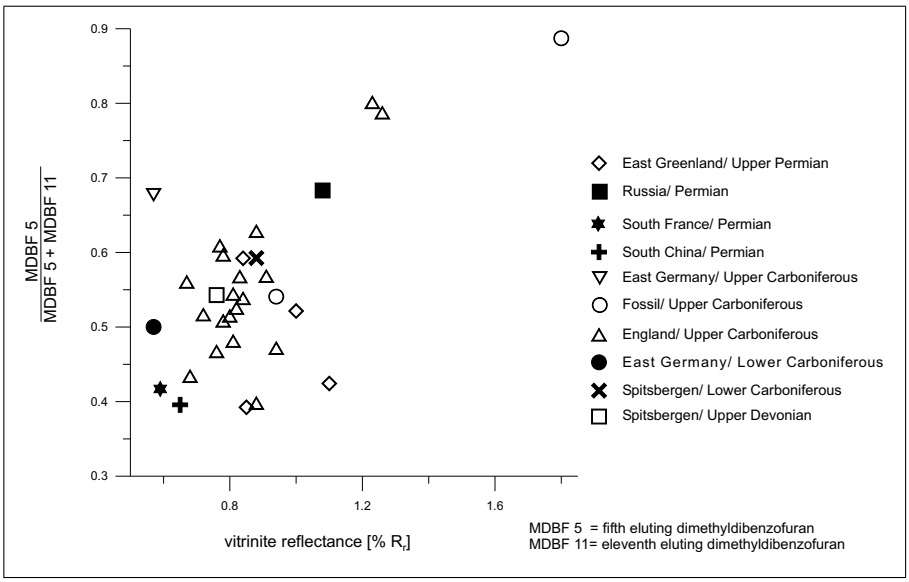

Figure 6.28: Cross plot of (MDBF 5)/(MDBF 5 + MDBF 11) *vs.* vitrinite reflectance

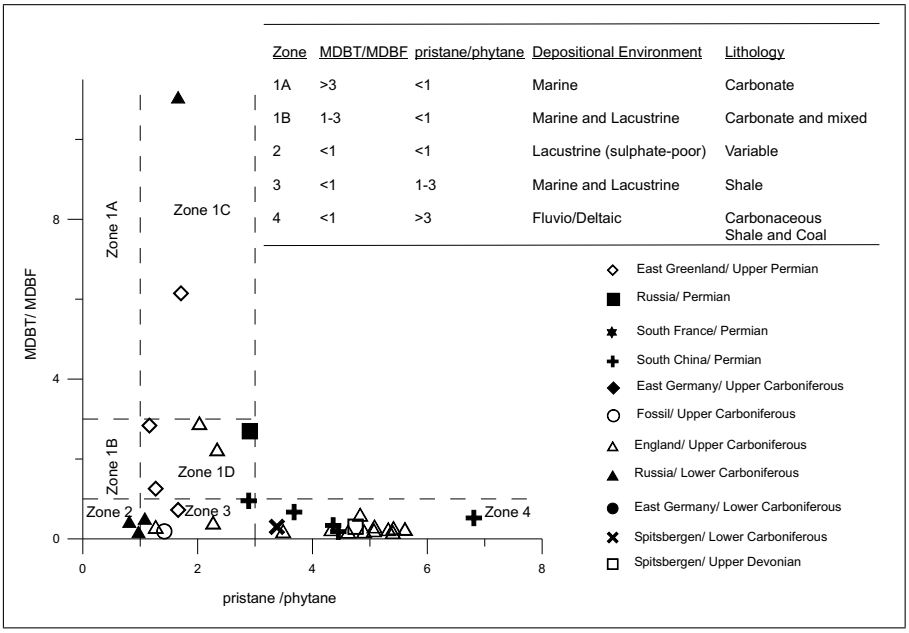

Figure 6.29: Cross plot of the ratio of methyldibenzothiophenes(excluding 1-methyldibenzothiophene)/methyldibenzofurans(excluding 1-methyldibenzofuran) *vs.* the ratio of pristane/phytane

Benzo[*b*]naphthofurans

Whereas benzocarbazoles have been applied as markers for secondary migration and maturity (Larter *et al.*, 1996; Clegg *et al.*, 1998b), nothing is known about the significance of benzo[*b*]naphthofurans. However, benzo[*b*]naphtho[*2,1-d*]-, benzo[*b*]naphtho[*1,2-d*]- and benzo[*b*]naphtho[*2,3-d*]furan are present in all investigated samples. The three compounds have been identified by coelution experiments using authentic standards. Normally the relative proportions of alkyldibenzofurans and benzo[*b*]naphthofurans are of the same magnitude. A fourth, later eluting compound additionally is present, showing a similar mass spectrum.

The relative proportions of the four compounds ranges from 2 to 374 μg/g TOC (Table A.31). Normally benzo[*b*]naphtho[*1,2-d*]furan and benzo[*b*]naphtho[*2,1-d*]furan are predominant (Fig. 6.30 A), while benzo[*b*]naphtho[*2,3-d*]furan is present in comparable magnitudes for the more immature samples only (Fig. 6.30 B). In contrast to the maturity trends observed for benzocarbazoles (Clegg *et al.*,

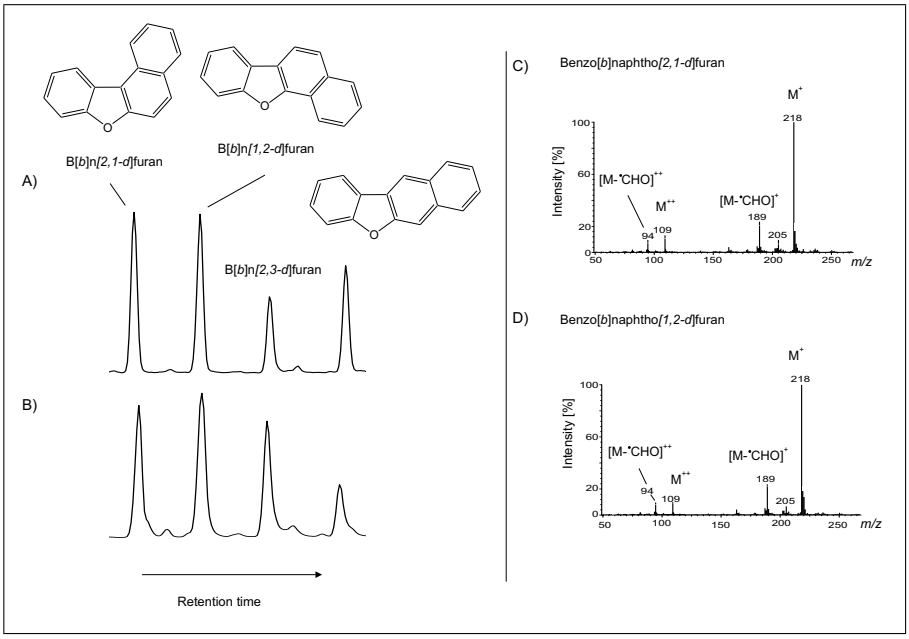

Figure 6.30: Gas Chromatogram of benzo[*b*]naphthofurans (*m/z* 218) in A) a Permian sample B) a Lower Carboniferous sample; and mass spectra of C) benzo[*b*]naphtho[*1,2-d*]furan and D) benzo[*b*]naphtho[*2,1-d*]furan indicating the similar fractionating pattern of these compounds

1998b), relative amounts of benzo[*b*]naphthofurans normally show no dependence on the maturity.

Carbazole and Alkylcarbazoles

Carbazole and alkylcarbazoles are constituents of crude oils and source rock extracts and make up a large portion of their organic nitrogen compounds (Helm

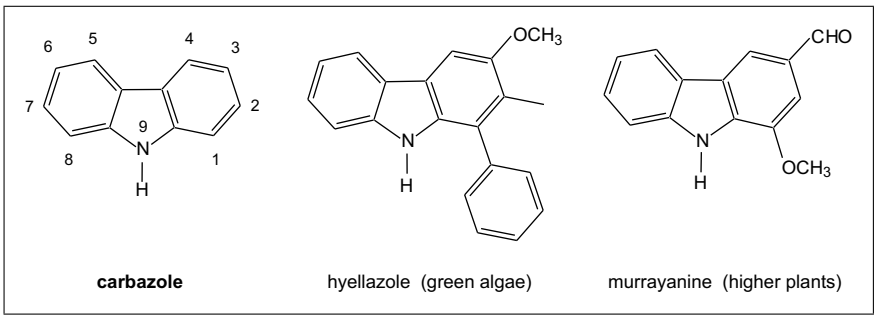

Figure 6.31: Carbazole and two alkaloids (Kapil, 1971; Hesse, 1974; Cardellina *et al.*, 1979) of different origin showing a carbazole skeleton

et al., 1960; Dorbon *et al.*, 1984; Bakel and Philp, 1990; Li *et al.*, 1997; Horsfield *et al.*, 1998). The primary discussion on these compounds in recent years is based on their potential as indicators of maturity and primary and secondary migration (Li *et al.*, 1994, 1995; Horsfield *et al.*, 1998; Clegg *et al.*, 1998a). The knowledge of their biological origin is limited.

It has been suggested that carbazoles (Fig. 6.31) might originate from alkaloids (Snyder, 1965) which are common constituents of blue-green algae (Cardellina *et al.*, 1979) and terrestrial plants (Kapil, 1971; Hesse, 1974). This origin has been discussed in detail by Li *et al.* (1995), and whereas the authors conclude, that alkaloids are not the major source of carbazoles they point out, that proteins and plant pigments might be a potential biological source. In contrast Dorbon *et al.* (1984) also line out, that alkaloids are no likely precursors of alkylcarbazoles, but suggest a complex formation mechanism involving the condensation of ammonia or low molecular weight amines.

Whereas the significance of the alkylcarbazole distribution as migration marker is questionable (Horsfield *et al.*, 1998; Clegg *et al.*, 1997), there seems to be an influence of facies and maturity (Clegg *et al.*, 1997). An increase of alkylcarbazoles with increasing thermal maturity has been observed for Posidonia Shale bitumen from Hils Syncline, northern Germany and crude oils from Thithonian source rocks in the Gulf of Mexico. However, the concentrations of alkylcarbazoles do not generally increase with maturity. In the Thithonian source rocks a decrease up to maturities of 0.81% R_r, followed by an increase at higher maturity ranges up to 1.09% R_r has been observed (Horsfield *et al.*, 1998; Clegg *et al.*, 1998b). Although several maturity parameters based on the isomeric distribution of alkylcarbazoles have been established (Li *et al.*, 1997; Clegg *et al.*, 1997, 1998b), none of them showed an unambiguous trend in general. Most recently Bakr and Wilkes (2002) suggested that the ratio of

$$\frac{(1,8-dimethylcarbazole)}{(1,8-dimethylcarbazole+1-ethylcarbazole)} \tag{6.3}$$

may depend on the environmental conditions. In crude oils from Egypt the authors found a slight correlation between this ratio and the pristane/phytane-ratio.

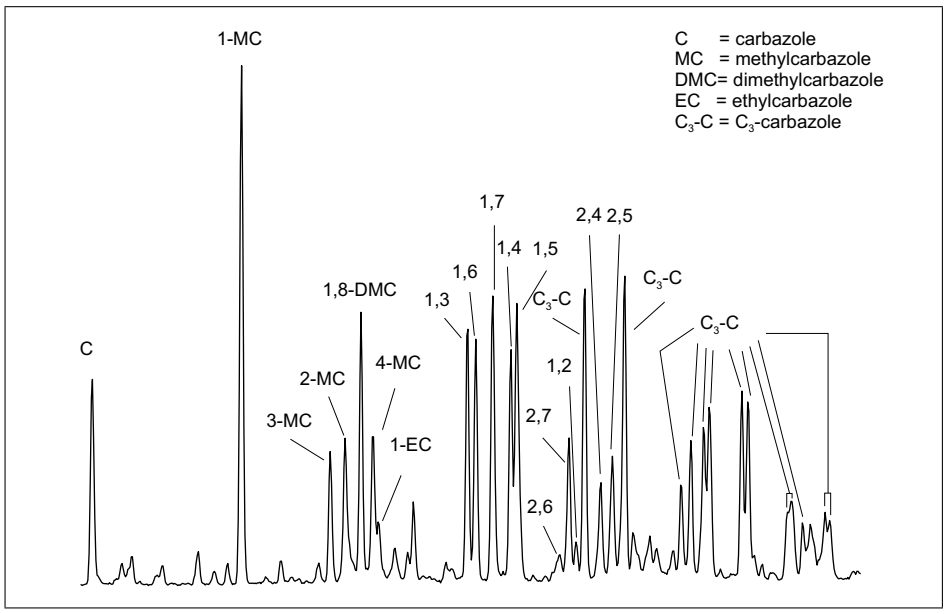

Figure 6.32: Gas Chromatogram of alkylcarbazoles (m/z 167, 181, 195, 209) in an Upper Carboniferous sample (for dimethylcarbazoles except 1,8-dimethylcarbazoles peaks are named via the position of the methylgroups due to lack of space in the chromatogram)

In the samples studied in this project alkylcarbazoles (Fig. 6.32) were assigned by comparison with mass spectra and published data (Bowler *et al.*, 1997). $C_{(0-3)}$-Carbazoles (Fig. 6.32) are present in most of the investigated samples. They were not detected in samples where the low-polarity fractions have generally been weak. Furthermore they were absent in immature samples, that additionally showed low values of the pristane/phytane-ratio.

For most of the samples the relative abundance of methylcarbazoles (MC) decreases in the following order: 1-MC>4-MC>2-MC>3-MC (Fig. 6.33A). This does not account for few samples only, which often are characterised by either relatively low maturities or high proportions of minerals. For these samples amounts of methylcarbazoles, except 1-methylcarbazoles are alike, while 1-methylcarbazole is still predominant. The ratio of 1,8-dimethylcarbazole/(1,8-dimethylcarbazole + 1-ethylcarbazole) shows only small variations for samples characterised by pristane/phytane ratios higher than 2.0 (Fig. 6.33B). Bakr and Wilkes (2002) investigated oils in which the ratio of pristane/phytane did not exceed values of 1.4. Obviously the ratio is not significantly influenced in samples that have been deposited under oxic conditions (pristane/phytane>3).

The distribution of dimethylcarbazoles, in correlation to the elevated proportions of 1-methylcarbazole, normally is also dominated by isomers, bearing a methyl group in the adjacent position to the nitrogen function. A predominance of these isomers has been reported previously (Frolov *et al.*, 1989). Again only few samples, characterised either by relatively low maturities or high amounts of minerals, show enhanced proportions of isomers exhibiting different substitution patterns. Besides these few exceptions, neither dimethylcarbazoles substituted in position 1- of the carbazole skeleton nor those showing no substitution at this position, are characterised by strong variations in relative amounts of individual isomers. The fact that alkylcarbazoles were absent in samples of very low maturities (0.31-0.65% R_r), except one may indicate that the compounds are formed by complex reactions, like has been suggested by Dorbon *et al.* (1984). However it may also result from environmental factors.

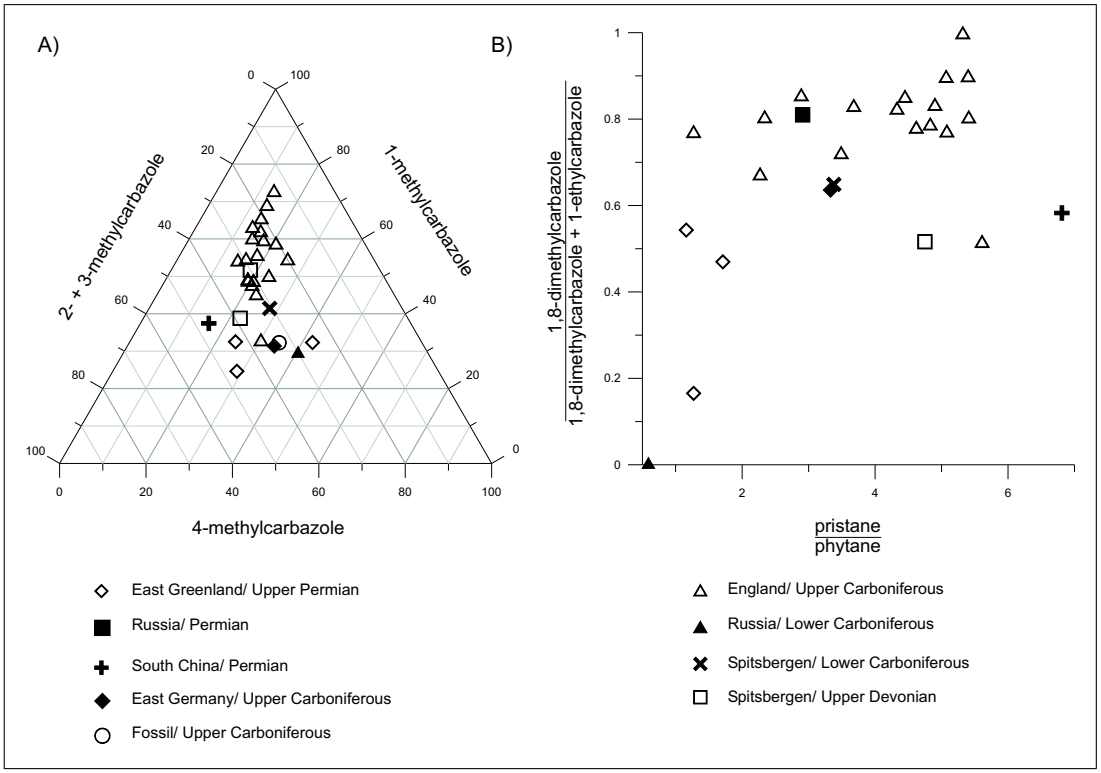

Figure 6.33: A) Ternary plot displaying the distribution of methylcarbazoles and B) plot of 1,8-dimethylcarbazole/(1,8-dimethylcarbazole + 1-ethylcarbazole) *vs.* pristane/phytane

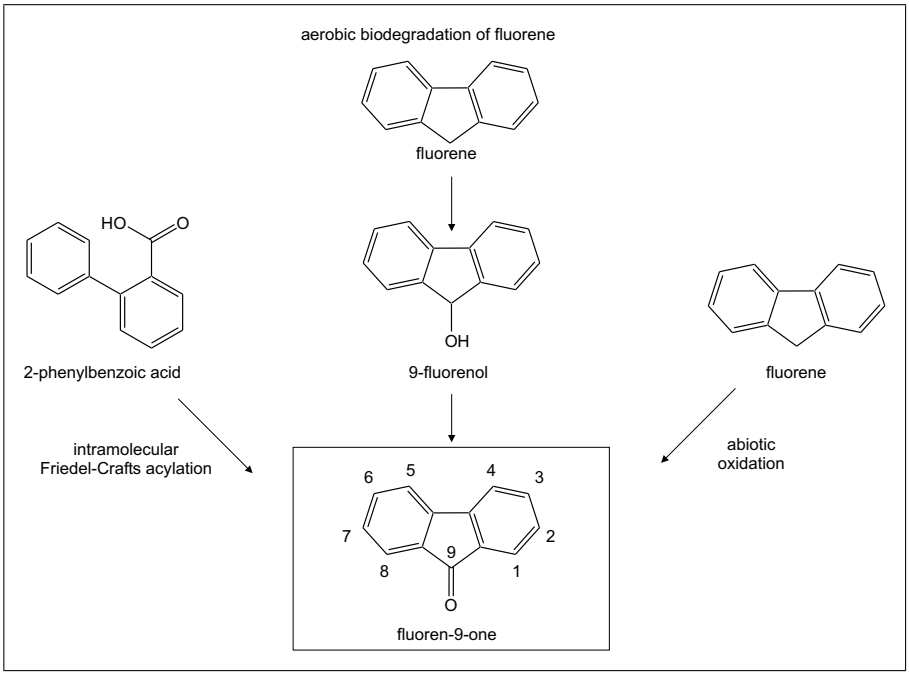

Figure 6.34: Possible pathways leading to the formation of fluoren-9-one

Fluoren-9-one and Alkylfluoren-9-ones

Studies on alkylfluoren-9-ones in both crude oils and sediments are rare. The compounds have been reported to be highly abundant in the low-polarity NSO compound fraction of Posidonia shales (Wilkes *et al.*, 1998a) and in extracts of reservoir cores (Bennett and Larter, 2000). Direct biological precursors of alkylfluoren-9-ones are unknown. However alkylfluorenes may be direct precursor of alkylfluoren-9-ones (Fig. 6.34). The benzylic carbon of the fluorene skeleton is activated and exposition of alkylfluorenes to sunlight in the presence of air yielded alkylfluoren-9-ones (pers. com. T. B. P. Oldenburg). Additionally fluoren-9-one is an intermediate and major product within the aerobic biological degradation of fluorene (Garon *et al.*, 2000; Eriksson *et al.*, 2000; Pothuluri *et al.*, 1993; Casellas *et al.*, 1997).

Cyclisation of 2-carboxybiphenyls via intramolecular Friedel-Crafts-reaction (Fig. 6.34) led to the formation of fluoren-9-ones (Wade Jr. *et al.*, 1979). This pathway has been suggested to play a major role in the formation of alkylfluoren-9-ones when depositional conditions are anoxic (Wilkes *et al.*, 1998a). Additionally

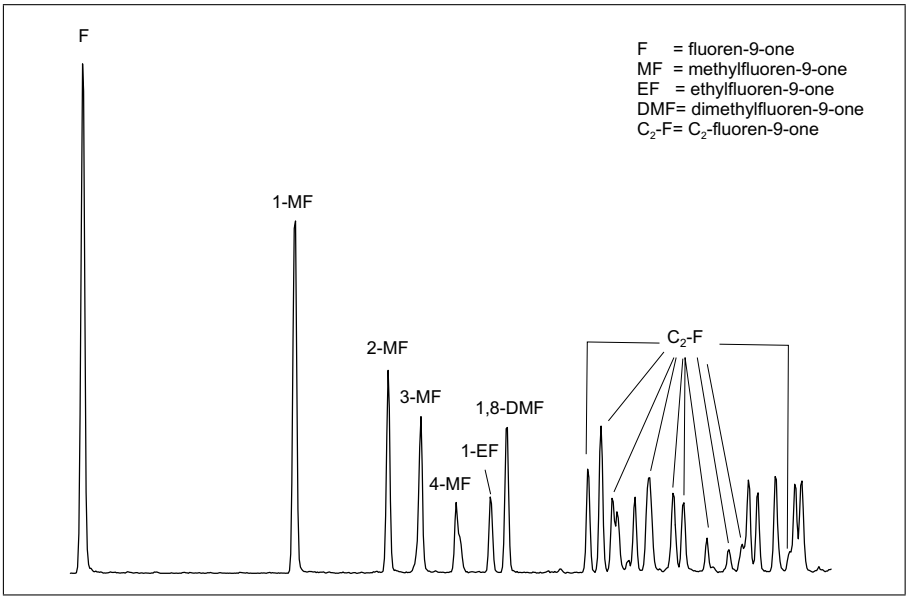

Figure 6.35: Gas Chromatogram of C_{0-2}-fluoren-9-ones (m/z 180, 194, 208) from an Upper Carboniferous coal

Davies and Waring (1968) observed the formation of fluoren-9-one via oxidation of *ortho*-benzylbenzoic acid in the presence of lead tetra-acetate.

In the samples studied in this project fluoren-9-one, methylfluoren-9-ones, 1-ethylfluoren-9-one and 1,8-dimethylfluoren-9-one (Fig. 6.35) have been assigned by mass spectra and comparison with published data (Wilkes *et al.*, 1998a). C_2-fluoren-9-ones have been identified by their mass spectra, but substitution patterns are unknown. Besides 1-ethylfluoren-9-one and 1,8-dimethylfluoren-9-one ten peaks were assigned to be C_2-fluoren-9-ones (Fig. 6.35). A coelution of isomers can not be excluded.

Alkylfluoren-9-ones normally were highly abundant in the low polarity NSO compound fraction. In contrast, alkylfluorenes were only minor contributors to the fractions of aromatic hydrocarbons. The distribution pattern of methylfluoren-9-ones and methylfluorenes to some extend are similar. 1-Methylfluoren-9-one, in analogy to 1-methylfluorene normally is the most abundant isomer, whereas 4-methylfluoren-9-one and 4-methylfluorene, respectively are least abundant. Variations in the distributions of alkylfluoren-9-one isomers for different samples normally are negligible. While fluorene was less abundant than methylfluo-

renes, fluoren-9-one strongly predominates over the methylfluoren-9-ones. The good correlation between relative amounts of methylfluorenes and corresponding methylfluoren-9-ones indicate a relationship between the two compound classes.

Xanthones

Xanthones are tricyclic aromatic compounds including an ether and a keto function within the ring system. Their occurrence in crude oils, i.e. fossil organic matter has been reported for the first time only very recently (Oldenburg *et al.*, 2002). Whereas unsubstituted xanthone is not known to occur in biogenic organic matter, poly-substituted xanthones are constituents of many terrestrial plants, which preferentially inhabit tropical or subtropical environments (Bennett and Lee, 1989; Peres and Nagem, 1997). They are known to be constituents of lichens, ferns and fungis. Oldenburg *et al.* (2002) suggested, that xanthones in fossil organic matter might be generated from these naturally occurring poly-substituted xanthones during diagenesis. Xanthone may also be formed via cyclisation of 2-phenoxybenzoic acid due to intramolecular Friedel-Crafts-reaction (Wade Jr. *et al.*, 1979).

Oldenburg *et al.* (2002) suggested that the relative amounts of xanthone, methylxanthones and C_2-xanthones depend on thermal maturity. The authors found a relative increase of xanthone concentrations in comparison to methylxanthone and C_2-xanthone concentrations at elevated maturities.

In the samples studied in this project xanthone and methylxanthones (Fig. 6.36) have been assigned by mass spectra and in comparison with published data (Oldenburg *et al.*, 2002). The relative amounts of 4-methylxanthone to some extend are not reliable due to coelution of this compound with a C_2-carbazole. C_2-Xanthones were not investigated, due to their low abundances.

Only few samples are characterised by the presence of xanthones. They correspond to a maturity range of 0.57-1.1% R_r. However xanthone and methylxanthones were not generally present in samples of this maturity range. The relative amounts of xanthone to methylxanthones showed no unambiguous dependence on the maturity of the samples. In analogy to methylcarbazoles and methylfluoren-

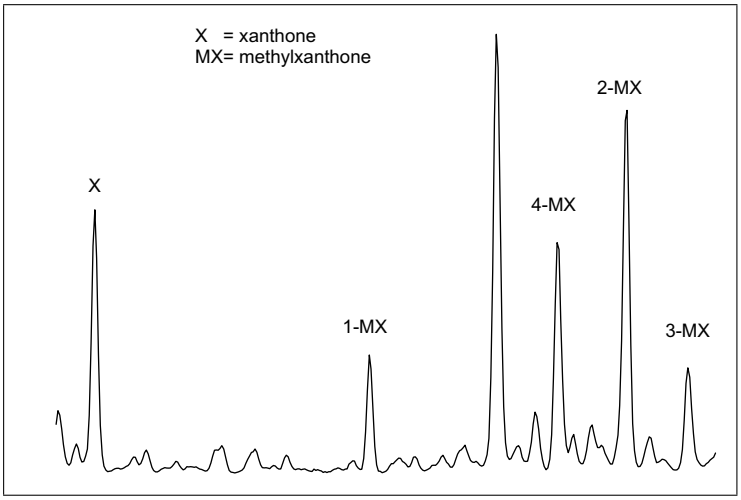

Figure 6.36: Gas Chromatogram of xanthone and methylxanthones (*m/z* 196, 210) from an Upper Carboniferous coal

9-ones variations of methylxanthone distributions for different samples are weak. Normally 2-methylxanthone (2-MX) is the most abundant isomer. Except for two samples the proportions of methylxanthones decrease in the following order: 2-MX>4-MX>1-MX/3-MX (Fig. 6.36). Again samples of low maturity show a different pattern. In these samples, 3-methylxanthone is relatively enriched. Besides the samples from East Greenland, the presence of xanthones is restricted to samples showing ratios of pristane/phytane >3.

Alkylnaphthaldehydes and Alkylnaphthylketones

Investigations on the occurrence of alkylnaphthaldehydes and alkylnaphthylketones (Fig. 6.37 A) in fossil organic matter are rare. The compounds were present in oil shales (Costa Neto *et al.*, 1980) and Posidonia shales (Wilkes *et al.*, 1998b). Wilkes *et al.* (1998b) for the first time investigated the geochemical significance of these compounds. The authors suggested, that alkylnaphthaldehydes and alkynaphthylketones may originate from alkylnaphthalenes. A formation via Friedel-Crafts acylation in the presence of clay minerals, serving as Lewis catalysts has been proposed. Additionally it has been suggested, that they may originate from oxidation of alkylsubstituted naphthalenes.

Maturity dependencies on the distribution of naphthaldehydes and alkynaphthylketones have been established on the base of six samples of the Posidonia shale. Wilkes *et al.* (1998b) observed an increase of the

$$\frac{(1--+2-naphthaldehyde)}{(1--+2-naphthaldehyde+1--+2-acetylnaphthalene)} \tag{6.4}$$

-ratio with increasing maturity.

$C_{(0-2)}$-Naphthaldehydes and $C_{(0-1)}$-alkylnaphthylketones are present in most of the investigated samples (Fig. 6.37 B). They are absent in samples characterised by weak fractions of low-polarity NSO compounds, only. Both 1- and 2-naphthaldehyde and 1- and 2-acetylnaphthalene have been assigned by comparison with mass spectra and published data (Wilkes *et al.*, 1998b). Higher homologues of these compounds were not identified in terms of their exact structure. However the isomers present in this study correspond well to the studies of Wilkes *et al.* (1998b).

For most of the samples 1- and 2-naphthaldehyde are the most abundant isomers of this compound class, comprising up to 50%. Compared to 1- and 2-acetylnaphthalene their relative abundance increases with increasing maturity for most of the samples. This does not account for samples showing high proportions of minerals, or maturities below 0.45% R_r. However, in contrast to the studies of Wilkes *et al.* (1998b) the relative amounts of naphthaldehydes in comparison to acetylnaphthalenes show no strong dependence on the vitrinite reflectance of the samples. Additionally, with few exceptions, the ratios are generally higher than the ones found by Wilkes *et al.* (1998b).

In analogy, the ratio of methylnaphthaldehydes to methylacetylnaphthalenes (Wilkes *et al.*, 1998b) also did not show a dependence on the maturity. Strongest deviations again were observed for samples of either low maturities or elevated proportions of minerals.

Except for one sample, 2-naphthaldehyde is generally more abundant than 1-naphthaldehyde. This corresponds to the relative proportions of 2-methylnaphthalene to 1-methylnaphthalene in the aromatic hydrocarbon fraction.

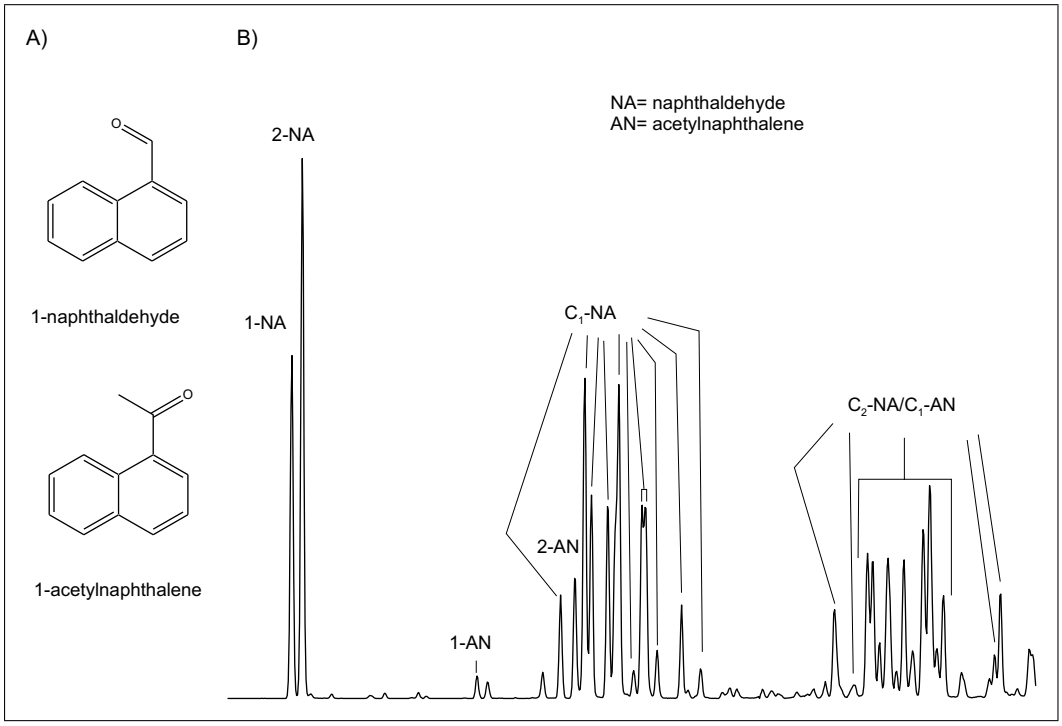

Figure 6.37: A) Structure of naphthaldehydes and acetylnaphthalenes and B) Gas Chromatogram of alkylnaphthaldehydes and -acetylnaphthalenes (m/z 156, 170, 184) from an Upper Carboniferous coal

The ratio of 2-naphthaldehyde to 1-naphthaldehyde, like the MNR shows no dependence on the maturity. Normally the distributions of methylnaphthaldehydes in different samples show only little variations. Nevertheless some samples show an enhanced concentration of the second eluting methylnaphthaldehyde. In samples, characterised by high proportions of minerals a relative enrichment of 1- and 2-acetylnaphthalene is observed. In correspondence to the findings for ethylnaphthalenes and methylnaphthalenes, the relative proportions of 2-acetylnaphthalene in comparison to 1-acetylnaphthalene show no dependence on maturity. In contrast the relative abundance of 2-acetylnaphthalene to 1-acetylnaphthalene for most of the samples is in good correlation to the relative abundance of 2-ethylnaphthalene to 1-ethylnaphthalene (Fig. 6.38). This in correspondence to the observations made for ethylnaphthalenes and methylnaphthalenes strongly indicates, that the distribution of this compounds is not controlled thermodynamically. Additionally a relationship between the aromatic hydrocarbons and their functionalised analogues is presumable.

Resumée

Alkyldibenzofurans and benzo[*b*]naphthofurans both are strong contributors to the extractable organic matter of many samples. The concentration of alkyldibenzofurans increases with increasing maturity, followed by a depletion for samples showing enhanced maturities. Additionally the compounds often are highly abundant in samples characterised by low maturities but high proportions of vitrinite. The findings support the hypothesis that alkyldibenzofurans are markers of terrestrial organic matter (Sephton *et al.*, 1999; Radke *et al.*, 2000). The distribution of some isomers indicates that the distribution of alkyldibenzofurans is influenced by maturity. An increase of 1-methyldibenzofuran, contrary to its relatively decreased thermal stability strongly indicates a specific biogenic contribution.

In contrast the distribution of benzo[*b*]naphthofurans shows no significant dependence on maturity. Neither an increase of this compound class in general is observed nor a strong variation in the relative proportions of different isomers. Their presence in all of the samples strongly indicates, that they are not formed due to elevated temperatures only. Additionally they often are present in same magni-

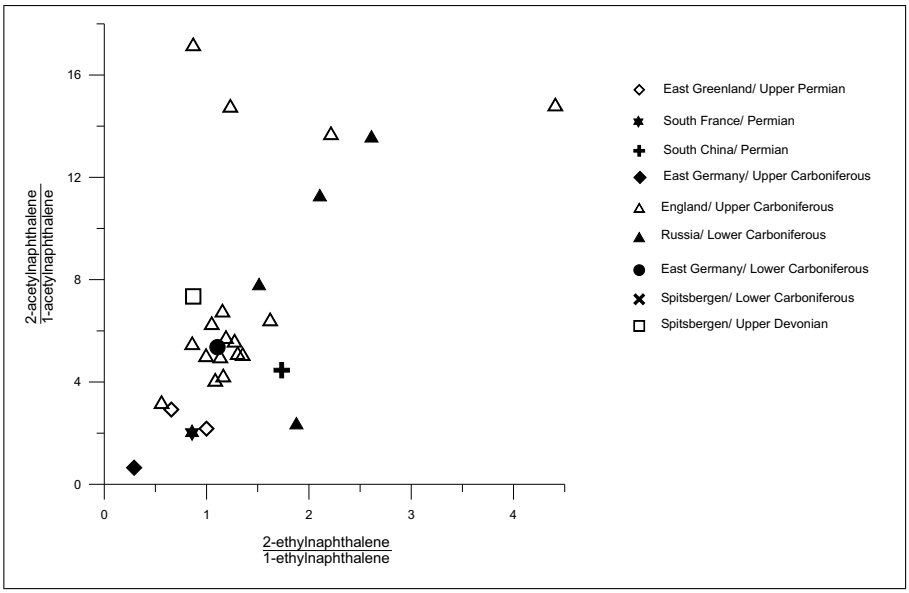

Figure 6.38: Cross plot of the ratios of 2-ethylnaphthalene/1-ethylnaphthalene *vs.* 2-acetylnaphthalene/1-acetylnaphthalene

tudes like alkyldibenzofuran, this strongly indicating, that they are not formed from alkyldibenzofurans due to condensation reactions.

Alkyldibenzothiophenes are minor contributors to the extractable organic matter. This strongly indicates, that conditions for the formation of these compounds have not been ideal. However the distribution of isomers for most of the samples shows a dependence on maturity. Additionally samples of elevated maturities often are characterised by elevated proportions of alkyldibenzothiophenes.

Alkylcarbazoles were absent in samples showing low pristane/phytane ratios and low maturities. The relative amounts of isomers for different samples, in contrast to alkyldibenzothiophenes does not vary significantly. The composition shows slight variations for more immature samples, which in addition are characterised by low pristane/phytane ratios. Nevertheless alkyl-1-methylcarbazoles generally are predominant.

In analogy to alkylcarbazoles, the composition of alkylfluoren-9-ones shows small variations for most of the samples. Alkylfluoren-9-ones were generally present and highly abundant in the low-polarity NSO compound fractions. The relative amounts of methylfluoren-9-ones show a good correlation to the corresponding alkylfluorenes. This in contrast is not observed for fluorene and fluoren-9-one.

Alkylxanthones, alkylnaphthaldehydes and -naphthylketones show slight correlation with maturity. Whereas alkylxanthones were only present in the maturity range of 0.57-1.1% R_r, naphthaldehydes and alkylnaphthylketones were present in a wider maturity range. Maturity trends normally are outlined by samples showing enhanced proportions of minerals or low maturity ranges. Relative amounts of methylnaphthaldehydes and naphthylketones show a correlation to certain aromatic hydrocarbons of the naphthalene skeleton.

6.4.2 Alcohols and Phenols

Introduction

Alcohols and phenols, i.e. compounds incorporating a hydroxy group as functional group are minor contributors to the extractable organic matter of the investigated samples. Because *n*-alkanes but also *n*-fatty acids have been strongly predominant in the specific fractions for most of the investigated samples, it is expectable that this is also due for *n*-alkanols. However, the proportions of alcohols and phenols generally are that low, that only significantly enriched homologues are recognisable. Besides these few *n*-alkanols, biphenols but also naphthalenemethanols were sometimes present. Likewise these compound classes were abundant to low proportions and in few samples only. Although hydroxy groups are often present in the original skeleton of natural constituents they indeed are less abundant than ketones, aldehydes, carboxylic esters and acids in sedimentary organic matter (Tissot and Welte, 1984).

Due to their low proportions alcohols and phenols were not investigated in detail. However, especially the presence of monoterpenes in samples of the Paleozoic has not been reported yet and therefore a short overview on their composition in the samples will be given.

Monoterpenoic Alcohols

Monoterpenoic alcohols have not been reported to occur in samples of the investigated geological age previously. The compounds are constructed from two C_5 isoprene units. They are abundant in higher plants and algae (Killops and Killops, 1993). Due to their high volatility and their odour they serve as herbivore defence but also as attractants. They are constituents of essential oils in plants. Monoterpenes for example isoborneol, borneol, fenchyl alcohol and camphor often show a strained bicyclic structure (Fig. 6.39). These compounds, besides terpineol were reported to occur in baltic amber (Tauber, 2000). In ambers they are bond to resin acids and are also suggested to be incorporated into macromolecules. Armstrong

et al. (1996) investigated chiral monoterpenoids in conifers and fossilized resins. The authors found borneol and isoborneol to be the most abundant monoterpenes in ambers, whereas in conifers monoterpenes like α-pinene and β-pinene were predominant.

In the investigated samples, besides the aromatic monoterpenes carvacrol and thymol, that will be discussed with other phenols, borneol, isoborneol, camphor, fenchyl alcohol, menthol, menthone and verbenone were abundant (Fig. 6.39). The compounds were identified by comparison with retention times and mass spectra of authentic standards. Although non-aromatic monoterpenes have been detected in samples ranging in age from Upper Devonian to Upper Permian and extend the maturity range of 0.37 to 1.8% R_r, only menthol, a monocyclic compound was abundant in samples of maturities beyond 1.08% R_r. Camphene, a possible dehydrogenation product of isoborneol and borneol (Armstrong *et al.*, 1996) was not found in the aliphatic fraction.

In their studies Armstrong *et al.* (1996) found similar ratios of borneol to isoborneol in most of the ambers investigated. Although the authors point out, that they only investigated a small amount of ambers, they suggest, that the ratio of borneol to isoborneol might reflect the early and later geochemical history of ambers (Armstrong *et al.*, 1996). The ratio of borneol to isoborneol in this study, in contrast to the studies of Armstrong *et al.* (1996) varies widely. However, it has to be considered that the organic matter studied here was not pure amber. Although the composition of monoterpenoic alcohols in the investigated samples may be of little significance, their presence in a sample of the Middle/Late Devonian indicates, that the capability to synthesize these compounds most probably predates the evolution of gymnosperms. For some immature samples, monoterpenes are highly abundant in the medium-polarity NSO compound fraction. The quantitative significance of the monoterpenes however is strongly limited by the high volatility of the compounds. Their presence in the samples probably does not represent their original amounts. A loss during sample preparation can not be excluded.

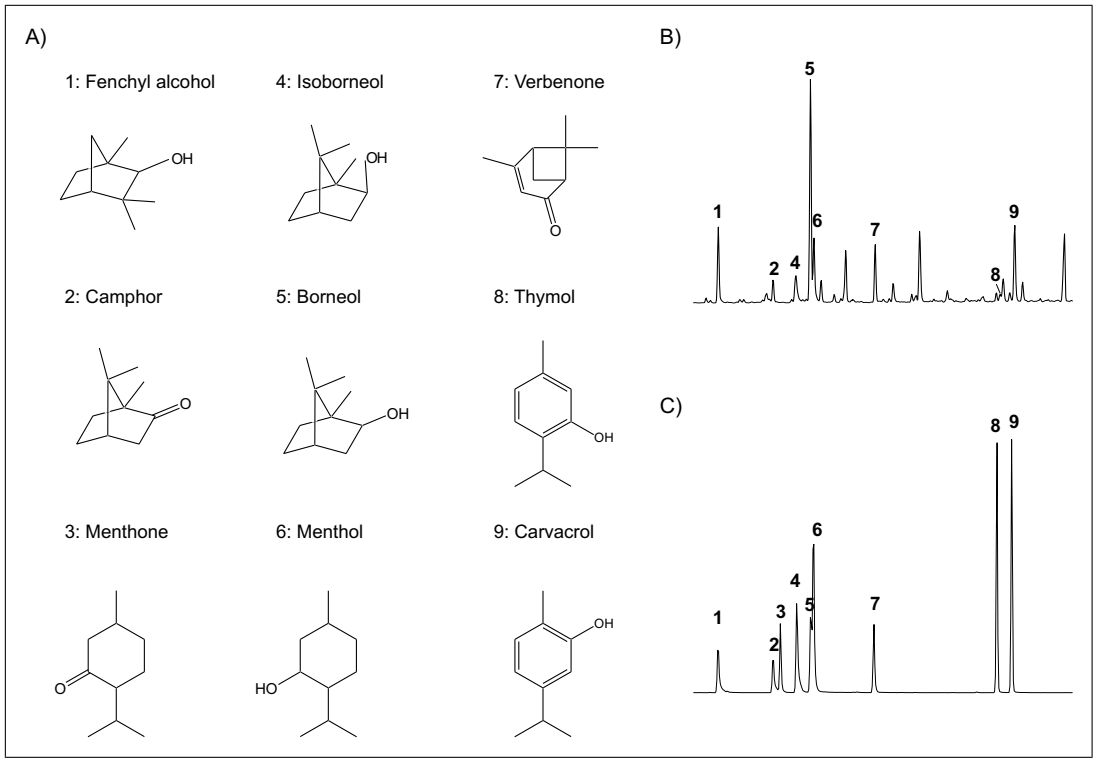

Figure 6.39: A) Structure of monoterpenes referred to in the text and B) the chromatogram (m/z 81, 95, 107, 112, 135) of an Lower Carboniferous sample and C) the chromatogram of a standard mixture

Table 6.8: Occurrence and composition of monoterpenes

Sample	Epoch	1	2	3	4	5	6	7
E 49748	Permian	+	-	n.d.	+	+	+	+
E 49749		+	-	-	+	+	-	+
E 49750		+	-	-	+	+	+	-
E 49751		+	-	-	+	+	+	-
E 48990		-	-	-	-	+	+	-
E 48397	Upper Carboniferous	-	-	-	-	+	+	-
E 48401		-	-	-	-	+	+	+
E 48383		-	-	-	+	+	+	+
E 48384		+	+	-	-	+	+	+
E 48986	Lower Carboniferous	+	+	-	-	+	-	+
E 48988		+	+	-	+	+	+	+
E 48989		+	+	-	+	+	-	+
E 48992	Upper Devonian	-	-	-	-	+	+	-

+:detected, -:not detected

Alkylphenols

Alkylphenols in general are widespread in nature and are constituents of lower and higher plants. They have been reported to be present in crude oils and sediments, where they have been investigated in detail (Ioppolo *et al.*, 1992; Ioppolo-Armanios *et al.*, 1994, 1995; Bennett *et al.*, 1996; Taylor *et al.*, 1997, 2001). The presence of many alkylphenols at least can be dated back to the Ordovician (Ioppolo *et al.*, 1992). Alkylphenols originate from different sources and may be natural products like carvacrol and thymol (Fig. 6.39). Ioppolo-Armanios *et al.* (1994) found the two monoterpenoic phenols in samples of the Permian. Such specific compounds occur especially in many families of angiosperms and gymnosperms (Ribereau-Gayon, 1972). They often are not present as free compounds but are bond as esters of glycosides or even more complex structures like lignins and tannins (Ribereau-Gayon, 1972). Besides in higher plants, phenols are also present in fungi (Ribereau-Gayon, 1972). Another possible source of alkylphenols is the alkylation of phenol and lower homologues. Indeed alkylation of phenols in the presence of acidic clays occurs faster than alkylation of aromatic hydrocarbons (Ioppolo-Armanios *et al.*, 1994, 1995). It especially results in the formation of *ortho*-alkylated isomers (Taylor *et al.*, 1997). Both, Ioppolo-Armanios *et al.* (1994, 1995) and Taylor *et al.* (1997) assume, that alkylphenols are predominantly formed in sediments due to these alkylation reactions. Phenols substituted in the *meta*-position on the other hand are the most stable isomers. They often are predominant in sediments and crude oils. This according to Ioppolo-Armanios *et al.* (1994) may result from isomerisation reactions. Although lignins and tannins, i.e. terrestrial organic matter are likely precursors, alkylphenols are often more abundant in type II kerogen than in type III kerogen (Taylor *et al.*, 1997). This correlates with the low proportions of hydroxylated compounds especially in more mature terrestrial organic matter.

Although a variety of alkylphenols has been identified in fossil organic matter (Ioppolo *et al.*, 1992; Ioppolo-Armanios *et al.*, 1994, 1995; Bennett *et al.*, 1996) interpretation is limited by the fact, that these compounds are volatile but also polar and that no relationship between concentration or distribution of alkylphe-

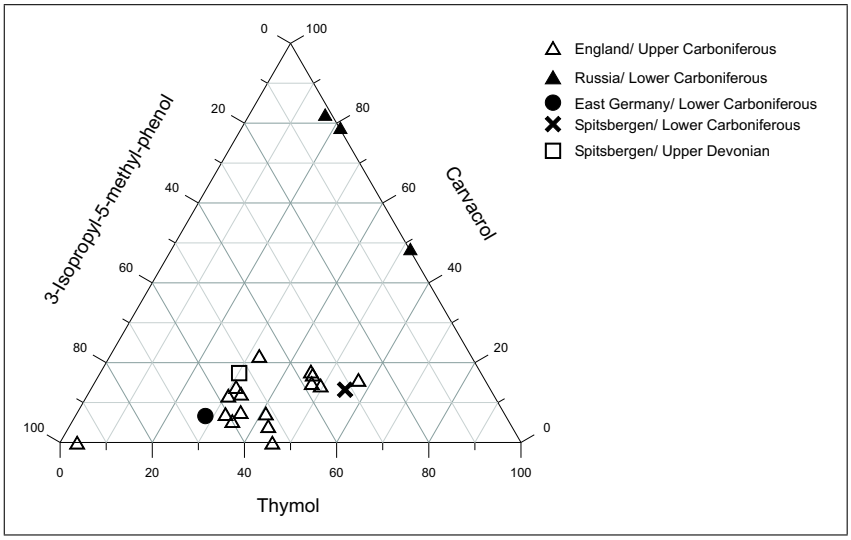

Figure 6.40: Ternary plot representing the distribution of thymol, carvacrol and 3-isopropyl-5-methylphenol

nols and maturity has been found (Ioppolo *et al.*, 1992). The elevated polarity of alkylphenols often results in their loss due to water washing (Lucach *et al.*, 2002).

For the samples investigated in the study of this project, the amounts and distribution of alkylphenols varies widely. As for the monoterpenes it can not be ruled out that a loss of alkylphenoles to different extents occurred before but also during sample preparation. However, carvacrol and thymol, which commonly co-occur in extant plants, are present in some samples and are of lower volatility and polarity than their lower homologues. Besides these two natural products, 3-isopropyl-5-methyl-phenol was often present. This compound has been suggested to be formed by rearrangement of thymol (Ioppolo-Armanios *et al.*, 1994). Thymol, carvacrol and 3-isopropyl-5-methyl-phenol were quantified in 23 samples extending the Upper Devonian to Upper Carboniferous period and the maturity range from 0.37 to 0.88% R_r. This time range clearly exceeds the one of Ioppolo-Armanios *et al.* (1994). In general relative concentrations of the three compounds do not vary significantly (Fig. 6.40). Normally 3-isopropyl-5-methyl-phenol is the most abundant isomer, whereas carvacrol is least abundant. In contrast samples of low maturity are characterised by the absence or low concentration of 3-isopropyl-5-methyl-phenol and a significant enrichment of carvacrol. The high proportions of carvacrol in immature samples indicate, that carvacrol might be an important

natural product for Late Paleozoic plants. It is presumable that a relative loss of carvacrol is due to the maturation of the organic matter. The relative depletion of carvacrol in correlation to the two other isomers however is not supposed to result from isopropylation. While methylation reactions are suggested to occur over a wide range of maturities, isopropylation reactions have only been observed in mature samples (Ioppolo-Armanios *et al.*, 1995). Due to the isopropyl group in carvacrol being at the more stable *meta*-position trans-isopropylation is not supposed to account for the depletion of carvacrol in more mature samples. The enhanced proportions of 3-isopropyl-5-methylphenol for samples of enhanced maturities in contrast may result from rearrangement reactions of thymol (Ioppolo-Armanios *et al.*, 1994). Due to the fact that a depletion of carvacrol in comparison to thymol probably is not the result of thermal transformations the changes in relative amounts are supposed to have another reason. It is probable that the significant depletion of carvacrol in comparison to thymol at enhanced maturities therefore may be the result of an additional source for thymol. Indeed aromatisation of menthol due to the stereochemistry of this compound would lead to the formation of thymol. This does also account for menthone. The latter compound may even be aromatisized more easily due to the keto-enol-tautomery present. Both compounds have been present in many of the investigated samples. Although at least menthol has been present over a wide maturity range it is possible that aromatisation of this compound partly occurs already at low maturity levels.

6.4.3 Carboxylic Acids

Introduction

Carboxylic acids are known to be constituents of crude oils, sediments and coals (Seifert, 1975; Hayatsu *et al.*, 1978a; Schmitter *et al.*, 1981). Investigations on carboxylic acids in fossil organic matter are mainly restricted to the group of fatty acids, i.e. saturated and unsaturated *n*-fatty acids, branched fatty acids, hydroxy fatty acids and α,ω-dicarboxylic acids, the group of hopanoic and steroidal acids (Lopes *et al.*, 1999; Hinrichs *et al.*, 1999; Murayama *et al.*, 1999) and resin derived acids (Anderson and Winans, 1991; Anderson and Botto, 1993; Anderson, 1994). Fatty acids normally are the most abundant compounds in acid fractions and are often considered because they have been proven to be biomolecules that frequently survive the transformations that occur during diagenesis.

Dehydroabietic acid is the most abundant diterpenoic acid in sediments of the northern hemisphere, and is a conversion product of abietic acid, present in resins of higher plants (Simoneit, 1986). Further carboxylic acids, that have been reported to occur frequently are methoxy- and hydroxybenzoic acids, which partly are constituents of lignin and therefore restricted to vascular plants (Hedges and Mann, 1979). Besides these compounds little is known about the occurrence of carboxylic acids showing aromatic skeletons in sediments and petroleum.

Apart from saturated *n*-fatty acids and hopanoic acids (Fig. 6.41), which were highly abundant in the investigated samples, the acid fractions also contain different classes of aromatic carboxylic acids. Whereas there is information about the origin of methoxy- and hydroxy-benzoic acids, little is known about the origin of phenanthrene- and anthracenecarboxylic acids, naphthalene- and naphthalenedicarboxylic acids (Fig. 6.41). Nevertheless they are known to be present in petroleum, sediments and coals (Seifert, 1975; Hayatsu *et al.*, 1978a).

An increase of acidic compounds has been observed with increasing biodegradation of oils (Behar and Albrecht, 1984). Increasing anaerobic degradation of petroleum hydrocarbons in groundwater environments also led to elevated levels of acidic com-

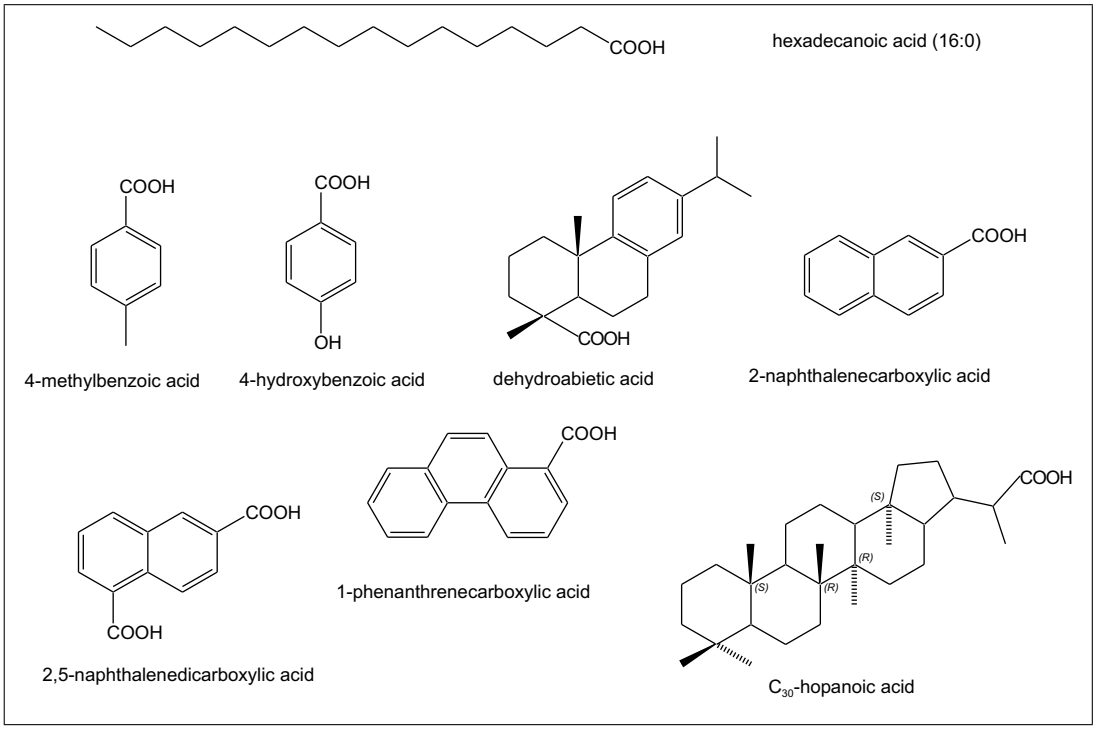

Figure 6.41: Acidic compound types present in the investigated samples

pounds (Cozzarelli *et al.*, 1990). On the other hand a formation of aliphatic and aromatic hydrocarbons from acidic precursors is known to occur during diagenesis, for example the conversion of abietic acid via dehydroabietic acid to retene.

Prior to gas chromatography/mass spectrometry the acid fraction of the samples investigated in the study of this project were methylated. While they were present as free acids before the identification bases on the esterfied compounds.

Saturated *n*-Fatty Acids

n-Fatty acids are abundant in most organisms and therein fulfil various functions. They are components of cellular membranes, serve as energy stores (for example in triglycerides) and protective coatings (for example in wax esters). *n*-Fatty acids normally possess an even number of carbon atoms, as they are formed from acetyl units (Killops and Killops, 1993). While *n*-fatty acids derived from animals are

saturated, acids originating from plants are either saturated or mono-, di-, tri- or polyunsaturated. Unsaturated fatty acids are more susceptible to biodegradation.

Saturated *n*-fatty acids in the range from C_{12}-C_{36} have been reported to occur in sediments and crude oils. The chain length of *n*-fatty acids to some extent is indicative for the biological origin. Saturated *n*-fatty acids with less than 20 carbon atoms are usually related to microorganisms and multicellular algae (Eglington *et al.*, 1968; Gong and Hollander, 1997). Nevertheless some of these short-chain *n*-fatty acids, like hexadecanoic (16:0) and octadecanoic (18:0) acid are ubiquitous (Volkman *et al.*, 1998) and do also occur in higher plants, for example in seed and leaf oils of gymnosperms (Vickery *et al.*, 1984; Aitzetmüller and Vosmann, 1998).

Saturated *n*-fatty acids, with more than 20 carbon atoms are attributed to cuticular waxes of higher plants (Cranwell, 1974; Eglington *et al.*, 1968), and are only produced in small amounts (<2%) by algae and bacteria (Volkman *et al.*, 1998).

The relative proportions of short-chain saturated *n*-fatty acids to long-chain saturated *n*-fatty acids (Wilkes *et al.*, 1999):

$$ATR_{FA} = \frac{(C_{14} + C_{16} + C_{18})}{(C_{14} + C_{16} + C_{18} + C_{26} + C_{28} + C_{30})} \tag{6.5}$$

may be used to estimate the origin of sedimentary organic matter. Values below 0.5 indicate a predominance of long-chain *n*-fatty acids originating from higher plants.

Carbon preference indices (CPI) have been introduced previously for *n*-alkanes. They serve to estimate the alteration in the *n*-fatty acid composition that has occurred during diagenesis and catagenesis:

$$CPI_{SFA} = \frac{1}{2}\left(\frac{\sum_{n=5}^{10} C_{2n}}{\sum_{n=5}^{10} C_{2n-1}} + \frac{\sum_{n=5}^{10} C_{2n}}{\sum_{n=5}^{10} C_{2n+1}}\right) \tag{6.6}$$

$$CPI_{LFA} = \frac{1}{2}\left(\frac{(C_{24} + C_{26} + C_{28} + C_{30})}{(C_{23} + C_{25} + C_{27} + C_{29})} + \frac{(C_{24} + C_{26} + C_{28} + C_{30})}{(C_{25} + C_{27} + C_{29} + C_{31})})\right) \tag{6.7}$$

CPI values significantly higher than one indicate, that the composition of *n*-fatty acids does not differ much from its original distribution. The CPI for long-chain *n*-fatty acids (CPI_{LFA}) is taken from Wilkes *et al.* (1999). Additionally a CPI for short-chain fatty acids (CPI_{SFA}) is used as some samples show only low amounts of long-chain *n*-fatty acids. The (CPI_{LFA}) for these samples due to the low amounts may be inexact. Whereas fatty acids in general seem to be relatively stable, Gong and Hollander (1997) presumed that long-chain saturated *n*-fatty acids are even more stable than short-chain saturated *n*-fatty acids.

Saturated *n*-fatty acids, ranging from C_7 to C_{32} were identified by their mass spectra. They normally are the most abundant compounds of the acid fraction for all samples. Whereas only few samples are characterised by an envelope distribution of the *n*-fatty acids (Fig. 6.42 C), most of the samples show a clear predominance of C_{14}-, C_{16}- and C_{18}- *n*-fatty acids (Fig. 6.42 B), and only few samples show a bimodal distribution with also high proportions of C_{26}-, C_{28}- and C_{30} *n*-fatty acids (Fig. 6.42 A).

The *n*-fatty acid distribution for most of the samples shows a clear even over odd predominance (Tab. 6.9). This predominance normally is more pronounced for short-chain *n*-fatty acids. The values indicate that the composition of the saturated *n*-fatty acids has been altered little by diagenesis and catagenesis. Nevertheless it should be mentioned, that few samples show an enhanced abundance of heptanoic (7:0) and nonanoic (9:0) acid. These short-chain *n*-fatty acids normally are not discussed in literature.

Except for three samples, values of the ATR_{FA} ranging from 0.5 to 1 (Tab. 6.9), indicate that long-chain *n*-fatty acids are minor contributors to the sum of *n*-fatty acids. Values at around one for most of the samples even indicate a strong predominance of short-chain *n*-fatty acids (Tab. 6.9). The predominance of long-chain *n*-fatty acids for three samples strongly correlates to their distribution of *n*-alkanes (Tab. 6.1).

The distribution of even-numbered C_{14}-C_{18} *n*-fatty acids normally is dominated by palmitic (16:0) acid, whereas stearic (18:0) acid is the least abundant (Tab. A.41). This distribution pattern is different for few samples only, which include the Per-

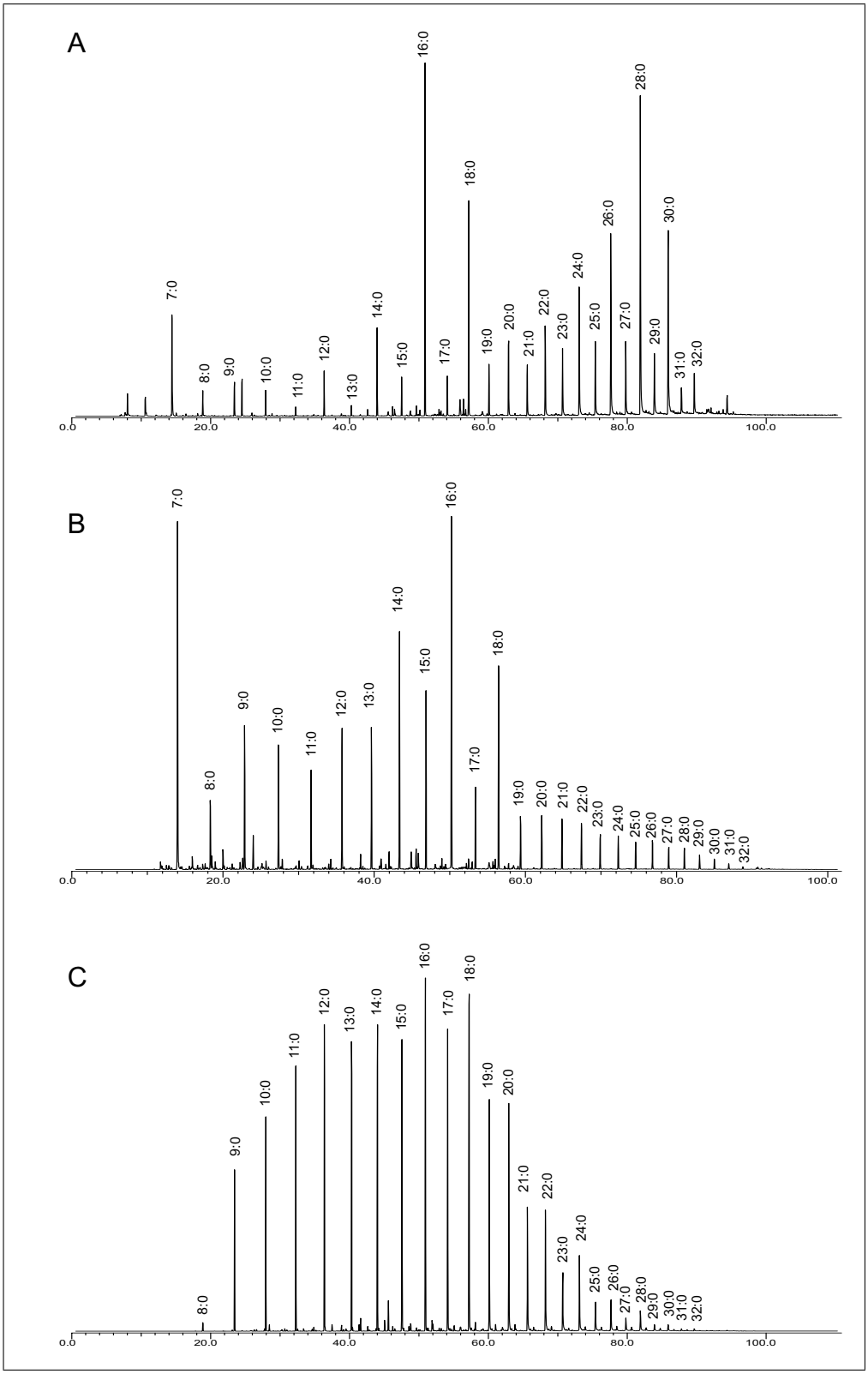

Figure 6.42: Distribution of *n*-fatty acids in sediments: A) Westphalian D, Saxony B) Westphalian B, Potato Pot, C) Viséan, Moscow Basin

Table 6.9: *n*-fatty acid ratios of the samples

Sample	CPI_{SFA}	CPI_{LFA}	ATR_{FA}	Sample	CPI_{SFA}	CPI_{LFA}	ATR_{FA}
E 49748	4.4	1.4	0.8	E 48394	3.4	-	-
E 49749	n.d.	n.d.	n.d.	E 48395	5.4	5.7	1.0
E 49750	7.2	3.9	1.0	E 48396	4.0	1.5	1.0
E 49751	1.9	2.1	0.8	E 48397	4.9	1.6	0.9
E 49710	17.9	-	-	E 48398	6.5	2.4	1.0
E 48990	10.5	1.4	1.0	E 48400	8.9	3.9	0.9
E 48478	1.2	1.1	0.8	E 48401	11.7	4.8	1.0
E 48479	1.3	1.1	0.7	E 48405	9.9	5.8	1.0
E 48480	4.5	1.8	1.0	E 48425	17.1	1.2	1.0
E 48996	4.5	2.6	0.3	E 48382	6.8	2.4	0.9
E 48388	2.6	1.5	0.9	E 48383	1.9	1.2	0.8
E 48389	2.9	1.4	0.9	E 48384	6.4	1.8	1.0
E 48390	3.3	1.3	0.9	E 48985	1.6	1.7	0.4
E 48214	2.4	1.2	0.9	E 48986	1.4	1.8	0.8
E 48216	2.1	1.1	0.9	E 48987	1.5	1.8	0.5
E 48403	7.6	5.1	1.0	E 48988	2.2	2.3	0.6
E 48220	2.8	1.4	0.9	E 48989	2.2	7.1	0.2
E 48430	5.5	-	-	E 48993	1.8	5.4	<0.1
E 48392	3.9	1.6	1.0	E 48991	12.1	1.6	1.0
E 48393	5.4	1.6	1.0	E 48992	5.8	2.1	0.9

mian and Westphalian age. Nevertheless little information can be gained by these distributions, as palmitic and stearic acid have been reported to be ubiquitous.

The distribution of even-numbered $C_{(26-30)}$-*n*-fatty acids, which are the most abundant within the long-chain saturated *n*-fatty acids, normally is dominated by hexacosanoic (26:0) acid, while triacontanoic (30:0) acid normally is least abundant (Tab. A.41). This does not account for few samples of the Permian and the Viséan period, only.

The low proportions of long-chain saturated *n*-fatty acids do not correspond to the terrestrial origin of organic matter for most of the samples. The high proportions of these compounds in two samples of the Viséan however indicate, that the opportunity to produce long-chain saturated *n*-fatty acids is a characteristic of this

period. Low proportions of long-chain saturated *n*-fatty acids in samples containing predominantly terrigenous material have been reported previously (Hinrichs and Rullkötter, 1997).

Alkylbenzoic Acids

Little has been reported about the occurrence of alkylbenzoic acids in fossil organic matter. Nevertheless some of them are constituents of plants and their presence in sediments may indicate which plants have contributed to the organic matter.

Benzoic acid is abundant in resins and essential oils of many plants (Karrer, 1976). It is also set free by the cleavage of alkaloids (cocaine, aconitine etc.) and glucosides (Karrer, 1976). Further alkylbenzoic acids that have been reported to occur in essential oils of plants are 4-methylbenzoic acid and phenylacetic acid (Karrer, 1976). Additionally alkylbenzoic acids are the main metabolites produced during anaerobic biodegradation of alkylbenzenes (Wilkes *et al.*, 2000; Cozzarelli *et al.*, 1990).

C_{0-2}-Alkylbenzoic acids, phenylacetic acids and phenylpropanoic acid were assigned by mass spectra and comparison with literature (Wilkes *et al.*, 2000). The compounds were present in the majority of the samples. It is suggested, that the first eluting dimethylbenzoic acid is 2,6-dimethylbenzoic acid. This is the only isomer that has not been identified in the literature (Wilkes *et al.*, 2000), and it is supposed to elute early due to its strong *ortho*-effect. Additionally one ethylbenzoic acid is present in many samples, which according to its retention time is either 4-ethylbenzoic acid or 3-ethylbenzoic acid. Quantifications of 2,4-, 2,3- and 3,5-dimethylbenzoic acids are sometimes not reliable due to coelution problems. Therefore the distribution of these three compounds has not been investigated.

Alkylbenzoic acids are present in most of the investigated samples. However their absence in some samples can not be attributed to a lack of these compounds in general. Due to their polarity it is also possible, that the compounds were lost by water washing in the sediments. This is supported by the fact, that samples lacking these compounds are neither characterised by high or low maturities, nor

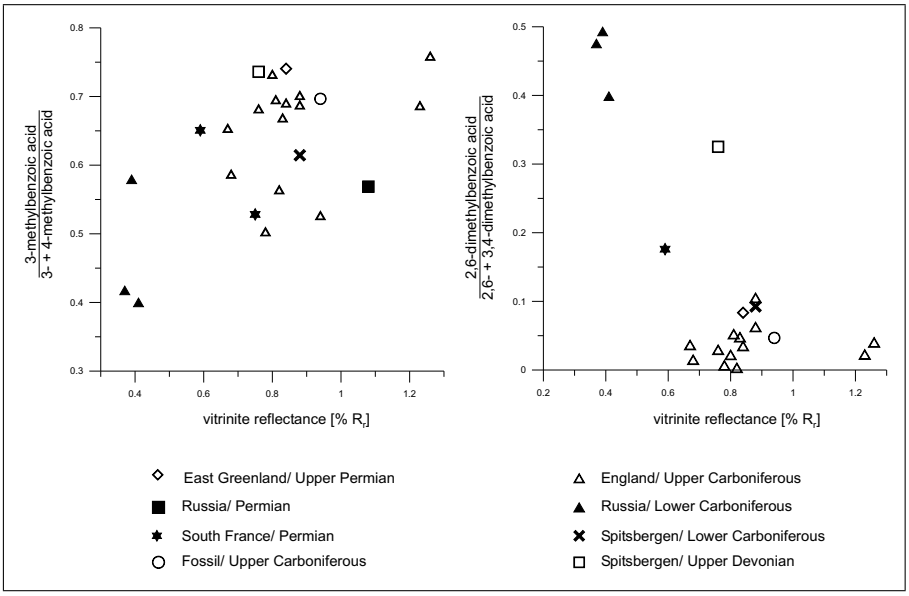

Figure 6.43: Maturity dependence of the distribution of methyl- and dimethylbenzoic acids

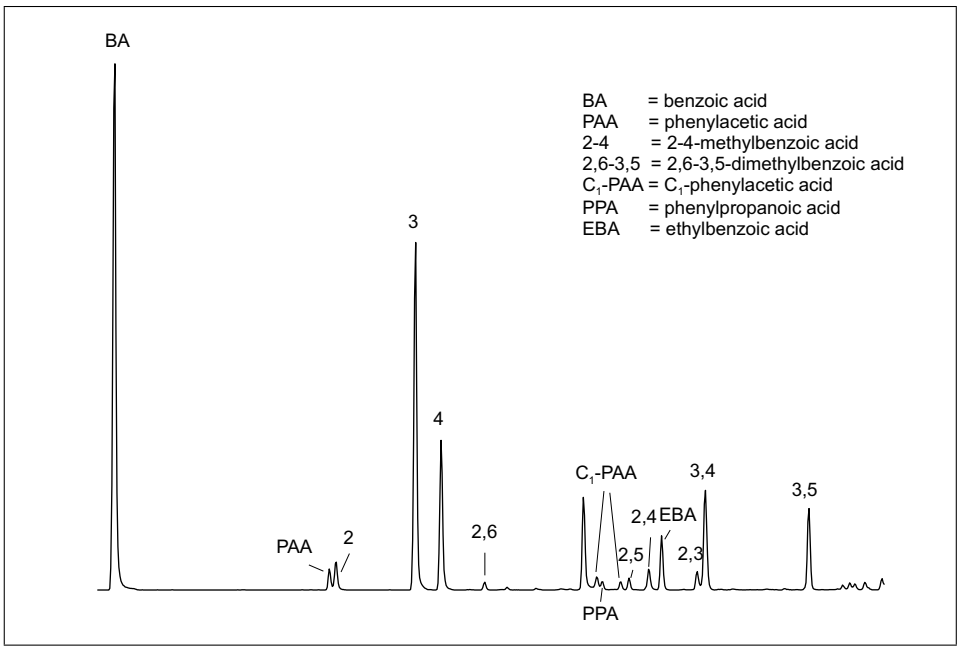

Figure 6.44: Gas Chromatogram of C_{0-2}-benzoic acids (m/z 136, 150, 164) in an Upper Carboniferous coal

by lack of a certain kind of maceral group. However one sample where vitrinite was not detected in microscopical investigations does show no presence of alkylbenzoic

acids, although there are high proportions of *n*-fatty acids in the earlier parts of the chromatogram.

Benzoic acid normally is highly abundant. In contrast 2-methylbenzoic acid and phenylacetic acid normally show low amounts in comparison to 3- and 4-methylbenzoic acid. Among the C_2-alkylbenzoic acids, generally 3,4- and 3,5-dimethylbenzoic acid are predominant. Additionally the ethylbenzoic acid present sometimes shows enhanced proportions.

The distribution of alkylbenzoic acids slightly correlates with maturity. With increasing maturity 3-methylbenzoic acid becomes the most abundant methylbenzoic acid. On the other hand, most of the more immature samples are characterised by relatively high proportions of 4-methylbenzoic acid. However, the relative increase in comparison to 4-methylbenzoic acid shows no unambiguous trend (Fig. 6.43 A). For immature samples 2,6-dimethylbenzoic acid often is highly abundant. The relative amounts of this compound in comparison to 3,4-dimethylbenzoic acid are only significantly enriched for the most immature samples (Fig. 6.43 B). The majority of the samples in contrast show low variations in the relative amounts of 2,6- and 3,4-dimethylbenzoic acid (Fig. 6.43 B). This correlates to the relative amounts of methylbenzoic acids (Fig. 6.43 A). Furthermore the first eluting methylphenylacetic acid and phenylpropanoic acid seem to slightly decrease with increasing maturity. The origin of phenylpropanoic acid is unknown, but compounds like cinnamic acid show a similar structure. Further isomers of benzoic acids show no significant decrease or increase in correspondence to maturity.

The distribution of the three phenylacetic acids show no similar pattern. Although this may be due to the relative low proportions for the two methylphenylacetic acids it does also indicate that there is no biogenic relationship between the three compounds. Especially the relative proportions of phenylacetic acid show only weak dependence on the maturity of the samples. The compound is highly abundant in samples characterised by low maturities, but is also generally highly abundant in samples of the Permian.

Lignin and Resin derived Acids

4-Hydroxybenzoic acid, 4-hydroxy-3-methoxybenzoic acid, 3,4-dimethoxybenzoic acid and compounds with up two three methoxy groups are normally attributed to lignin and therefore are indicators of terrestrial organic matter (Stefanova and Disnar, 2000). The magnitude of methoxylation and hydroxylation correlates to the origin of lignin. The absence of syringyl acids, i.e. 3-hydroxy-2,4-dimethoxybenzoic acid is usually interpreted as an evidence that the lignin derives from non-woody gymnosperm/angiosperm tissues.

Some hydroxy-/methoxybenzoic acids are also constituents of essential oils. 2-Hydroxybenzoic acid (salicylic acid) for example has been reported to be present in many essential oils of different plant types (Karrer, 1976). This does also account for 2-methoxybenzoic acid. 4-Hydroxybenzoic acid is a constituent of leaves and blooms in several plants, whereas 6-alkyl-4-methoxybenzoic acids are present in extracts from several woody constituents of for example *Gingko biloba* (Karrer, 1976).

Additionally salicylic acid but also 4- and 5-methylsalicylic acid are products within the aerobic biodegradation of 2-methylphenanthrene (Budzinski *et al.*, 2000; Sabaté *et al.*, 1999). Phenanthrene and further methylphenanthrenes are probably biodegraded via the same pathway. Salicylic acid is also produced during aerobic biodegradation of dibenzofuran (Fortnagel *et al.*, 1989, 1990). The biodegradation of alkylnaphthalenes does also result in the formation of these compounds (Dutta *et al.*, 1998). Due to the high polarity of these compounds, they may be lost by water washing (Mackenzie *et al.*, 1983). Additionally, the relatively enhanced volatility of the lower isomers may strongly influence individual samples to different amounts. The composition found in the samples therefore does not necessarily represent the composition prior to sample preparation.

Like methoxy- and hydroxy benzoic acids, diterpenoic acids are derived from terrestrial contributors, i.e. resins. It was mentioned previously, that dehydroabietic acid is the most abundant diterpenoic acid of sediments in the northern hemisphere. This is due to the fact, that the abietane type is the predominant diter-

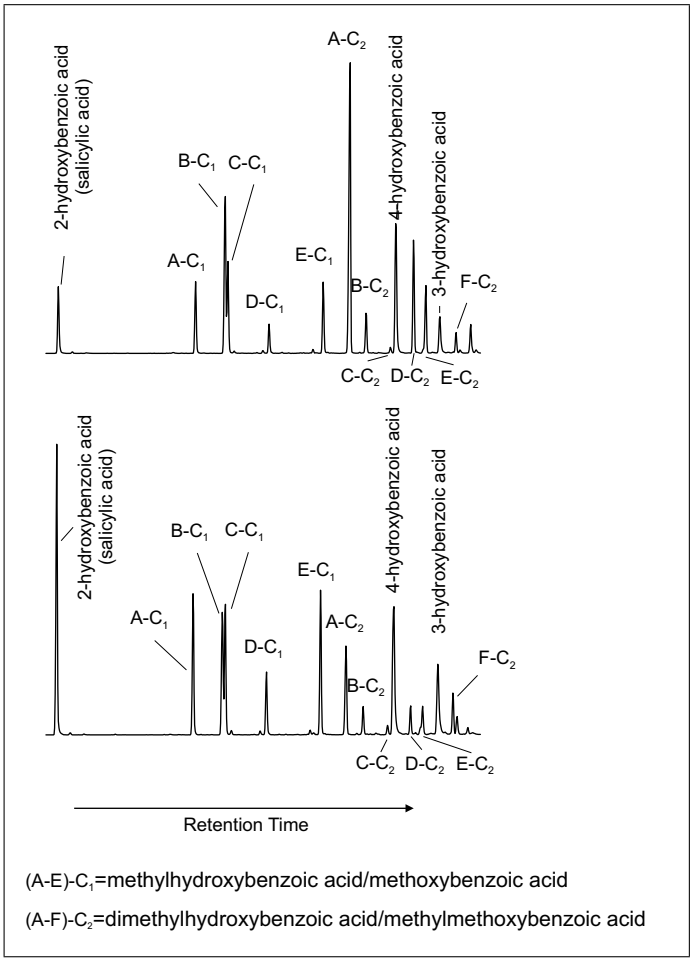

Figure 6.45: Gas Chromatograms of alkylhydroxy-/-methoxybenzoic acids (m/z 152, 166, 180, 196) of two Upper Carboniferous coals. The two coals are characterised by a similar vitrinite reflectance. The strong variations in the amounts of alkylhydroxy-/-methoxybenzoic acids strongly indicate that neither maturity nor geological age are the main factors influencing their composition

penoic skeleton for example in Pinus (Thomas, 1970). Dehydroabietic acid is a conversion product of abietic acid, that is formed in resins in situ (Simoneit, 1986). Additionally resins often contain lignin derived compounds (Thomas, 1970).

Hydroxybenzoic acids, 4-hydroxy-3-methoxybenzoic acid, 3,4-dimethoxybenzoic acid and diterpenoic acids were identified according to their mass spectra. Besides the three hydroxybenzoic acids, eight methoxy-/methylhydroxybenzoic acids have been identified and six compounds that may be either methylmethoxybenzoic acids or dimethyl-/ethylhydroxybenzoic acids.

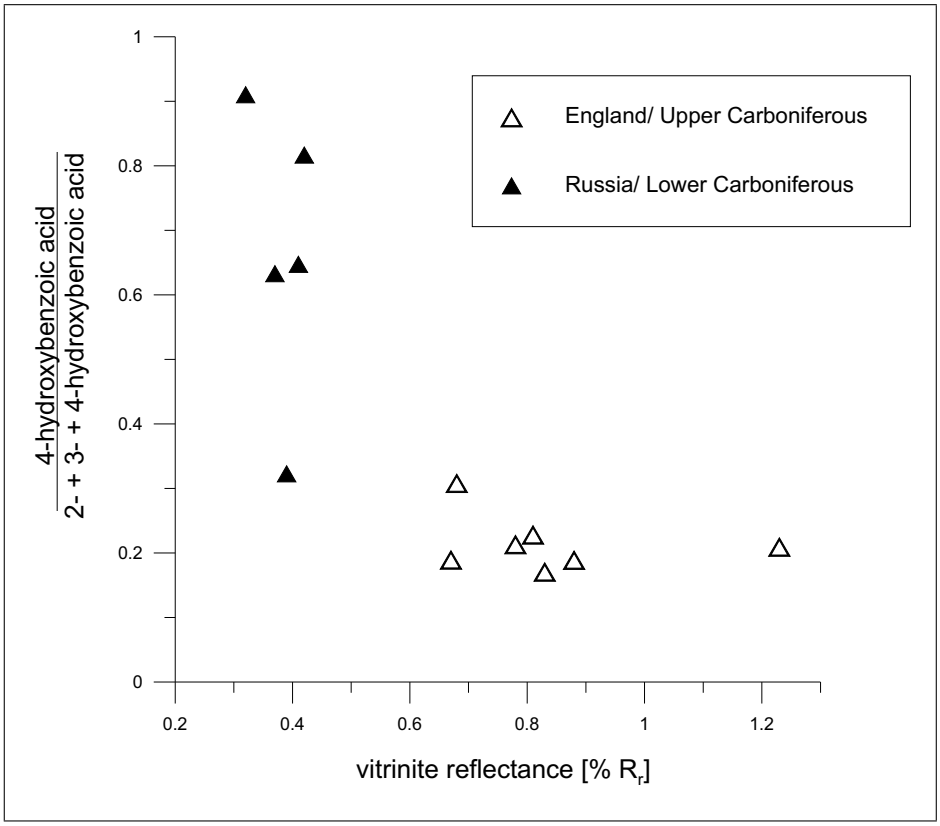

Figure 6.46: Cross plot displaying the ratio of 4-/(2- + 3- + 4-)hydroxybenzoic acid *vs.* the vitrinite reflectance

Whereas 4-hydroxy-3-methoxybenzoic acid, 3,4-dimethoxybenzoic acid and dehydroabietic acid are present in most of the samples, alkylmethoxy-, alkylhydroxybenzoic acids and further diterpenoic acids often are absent.

Hydroxybenzoic acids and higher homologues were abundant in most of the Upper Carboniferous samples originating from England, and in the five samples of the Lower Viséan from Moscow Basin. The maturity of these samples extents the range of 0.32-0.88% R_r. For many of these samples 2-, 3- and 4-hydroxybenzoic acid have been the only isomers present, while higher homologues often are absent or present in minor amounts. This does especially account for the immature samples from the Moscow Basin.

The distribution of hydroxybenzoic acids shows a slight dependence on maturity. While 4-hydroxybenzoic acid is present in high amounts in the more immature sam-

ples, 3- and 2-hydroxybenzoic acid are significantly predominant in the more mature samples (Fig. 6.46). The high amounts of 4-hydroxybenzoic acid in samples of low maturity corresponds to its biogenic significance. 4-Hydroxybenzoic acid is related to coumaryl type constituents of lignin. Compounds of the coumaryl type however are normally present in higher plants and their presence in samples of the Carboniferous are expectable. In contrast to 4-hydroxybenzoic acid, 4-hydroxy-3-methoxy- and 3,4-dimethoxybenzoic acid were present in samples extending the time range from Late Devonian to Permian and the maturity range from 0.32% to 1.26% R_r. The fact, that the two compounds have been present in a Devonian sample where 4-hydroxybenzoic acid has been absent, may indicate that the biological origin of monohydroxy-/monomethoxybenzoic acids and 4-hydroxy-3-methoxy- and 3,4-dimethoxybenzoic acid is not the same.

In general the distribution of hydroxy- and methoxybenzoic acids and their higher homologues varied widely for the samples, not indicating a strong biogenic relationship. 4-Hydroxy-3-methoxy- and 3,4-dimethoxybenzoic acid have additionally been absent in samples characterised by high CPI values of long-chain *n*-alkanes and -fatty acids.

Abietic acid was only present in one sample of the Upper Carboniferous. This sample is characterised by the absence of 4-hydroxy-3-methoxy- and 3,4-dimethoxybenzoic acid. Diterpenoic acids of the pimarane type were present in few samples ranging from the Lower Carboniferous to the Permian including the maturity range of 0.32 to 1.80% R_r. Dehydroabietic acid is by far the most abundant resinous acid, present in all samples from Upper Devonian to Permian, except for three samples, where acidic compounds could merely be characterised, and the sample from South China, which does not belong to the Euramerian flora realm.

Alkylnaphthalenecarboxylic Acids

Although alkylnaphthalenecarboxylic acids are known to be present in coals (Hayatsu *et al.*, 1978a), no investigations with respect to their relative proportions and distribution have been carried out. Alkylnaphthalenecarboxylic acids in the range of C_0-C_3 were detected in some of the investigated samples. Due to low proportions

and coelution problems of higher homologues only C_{0-1}-naphthalenecarboxylic acids were quantified. The compounds were identified by mass spectra and comparison with literature (Zhang and Young, 1997). The mass spectra of 1- and 2-naphthalenecarboxylic acid are characterised by a strong m/z 186 (M^+), 155 (M^+-CH_3O) and 127 (M^+-$COOCH_3$). The mass spectra of C_1-naphthalenecarboxylic acids are characterised by a strong m/z 200 (M^+), 169 (M^+-CH_3O) and 141 (M^+-$COOCH_3$). Besides 1- and 2-naphthalenecarboxylic acid, no further isomer has been identified unambiguously. Nevertheless, 11 C_1-naphthalenecarboxylic acids could be detected.

While the compounds were present in 17 samples in general, small amounts of 2-naphthalenecarboxylic acid were also present in samples, that lack other homologues. The samples where the complete set of $C_{(0-1)}$-naphthalenecarboxylic acids was present extend the time range from Upper Devonian to Permian and the maturity range of 0.41 to 1.26% R_r.

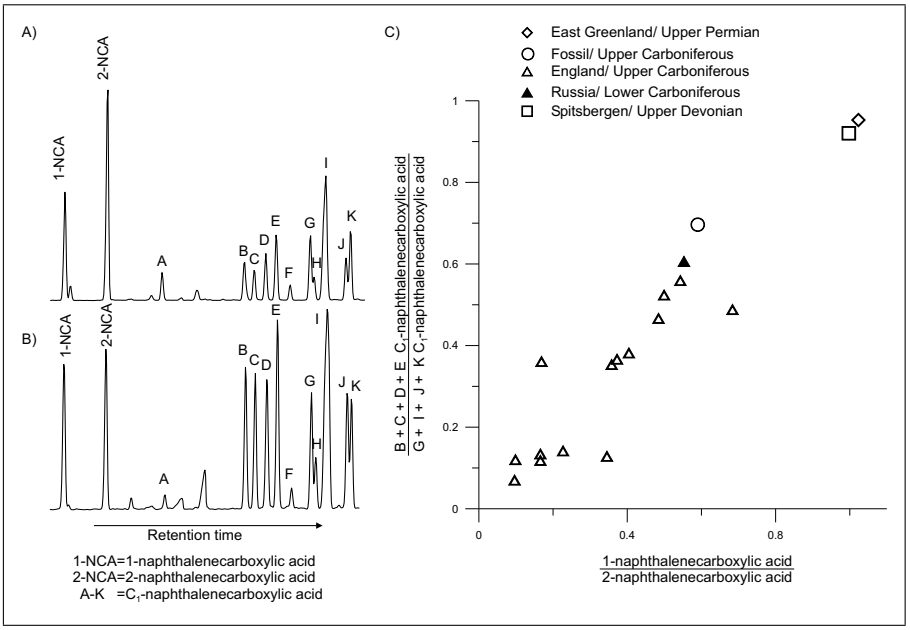

Figure 6.47: Gas Chromatograms of C_{0-1}-naphthalenecarboxylic acids of A) an Upper Carboniferous coal and B) the Upper Permian sediment from East Greenland; and C) Cross plot displaying the ratio of (1-/2-)naphthalenecarboxylic acid to the ratio of selected C_1-naphthalenecarboxylic acids

The presence of alkylnaphthalenecarboxylic acids is not restricted to the presence of a certain maceral group or a certain maturity range. Their composition does not vary significantly. Normally 2-naphthalenecarboxylic acid is present in major proportions compared to 1-naphthalenecarboxylic acid (Fig. 6.47 C). This does also account for the later eluting C_1-naphthalene carboxylic acids, in comparison to isomers eluting more early (Fig. 6.47 A and C). This strongly indicates that C_1-naphthalenecarboxylic acids B-E are C_1-1-naphthalenecarboxylic acids while isomers G-K are C_1-2-naphthalenecarboxylic acids (Fig. 6.47 A and B). The only two samples where C_{0-1}-1-naphthalenecarboxylic acids are relatively enriched are characterised by enhanced proportions of liptinites (Fig. 6.47 B and C).

Alkylnaphthalenedicarboxylic Acids

The occurrence of alklynaphthalenedicarboxylic acids in fossil organic matter has not been reported in the literature. In contrast their presence in contaminated soils is known. The degradation of phenanthrene resulted in the formation of 1,2-naphthalene dicarboxylic acid as by-product (Richnow *et al.*, 2000).

In the acid fraction of some samples three compounds were present, that by comparison with standards of 2,6-, 1,4- and 2,3-naphthalenedicarboxylic acids, probably are also naphthalenedicarboxylic acids but none of the standard compounds. Additionally seven compounds, that based on their mass spectra might be C_1-naphthalenedicarboxylic acids (Fig. 6.48 A), and four compounds that might be C_2-naphthalenedicarboxylic acids (Fig. 6.48 A) were detected.

The complete set of these compounds was present in 17 of the investigated samples, which are not fully but often identical with the ones where naphthalenecarboxylic acids were present. Alkylnaphthalenedicarboxylic acids are generally absent in samples of the Permian. They are present in the maturity range of 0.67 to 1.23% R_r.

Among the C_1-naphthalenedicarboxylic acids, the first eluting one shows a slightly different mass spectrum. In comparison to the other isomers it is characterised by a weak m/z 227 (M^+-CH_3O) but a strong m/z 213 (possibly M^+-C_2H_5O).

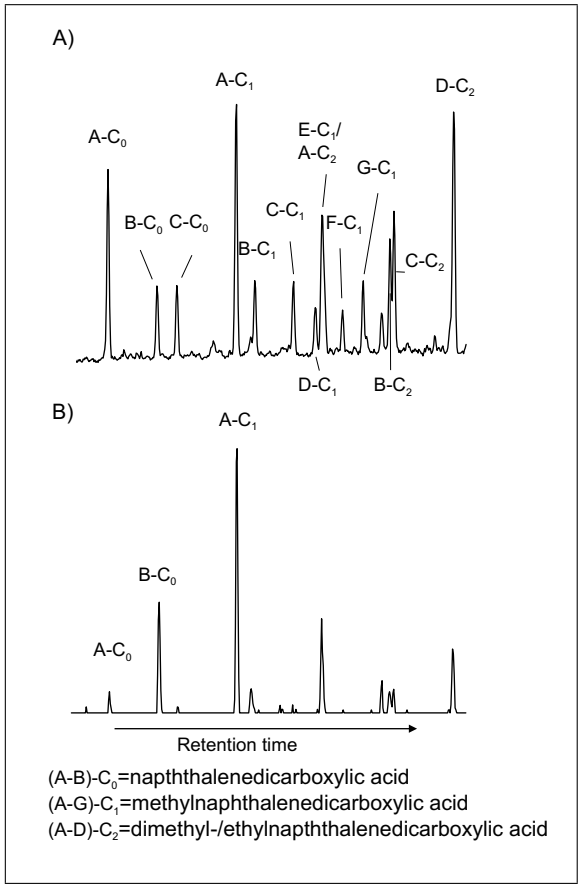

Figure 6.48: Gas Chromatograms of $C_{(0-2)}$-naphthalenedicarboxylic acids (m/z 244, 258, 272) A) in a sample from the Upper Carboniferous, where all isomers are present and B) in the Devonian sample, where only few isomers are present in detectable amounts

M^+ (m/z 258) was strong for all five isomers. The different mass spectrum of the first eluting C_1-naphthalenedicarboxylic acid strongly indicates that it prior to derivatisation has been a naphthalenedicarboxylic acid-monoethylester.

While the distribution of C_2-naphthalenedicarboxylic acids generally does not vary significantly, the samples can be divided into two groups based on the distribution of C_{0-1}-naphthalenedicarboxylic acids. The first eluting C_1-naphthalenedicarboxylic acid is always present in the samples and often the most abundant compound. Nevertheless the relative proportions seem to be enhanced for samples where the second eluting C_0-naphthalenedicarboxylic is also relatively enriched (Fig. 6.48 B). Other C_1-naphthalenedicarboxylic acids often are depleted in these samples. The two compounds are also present in samples of the Viséan

and the Upper Devonian, that lack the other isomers of this compound class. Five samples on the other hand are characterised by low amounts or the absence of the second eluting C_0-naphthalenedicarboxylic acid. Additionally they show high proportions of later eluting C_1-naphthalenedicarboxylic acids, while the first eluting C_1-naphthalenedicarboxylic acid is not necessarily depleted (Fig. 6.48 A). Based on the clear subdivision into two groups of samples it may be proposed, that the detected alkylnaphthalenedicarboxylic acids originate from at least two different sources.

Alkylphenanthrene- and Alkylanthracenecarboxylic Acids

The possibility, that phenanthrene carboxylic acids are constituents of petroleum and sediments has first been mentioned by Seifert (1975), who did not propose, that anthracene carboxylic acids might also be present.

Alkylphenanthrene- and alkylanthracenecarboxylic acids were detected in 19 of the investigated samples. Besides three samples, these samples are identical with the ones, where naphthalenecarboxylic acids were detected. The samples where alkylphenanthrene-/anthracenecarboxylic acids were present extend the time period from Upper Devonian to Permian and the maturity range of 0.59-1.26% R_r. Besides five C_0-phenanthrene-/anthracenecarboxylic acids, 12 C_1-isomers were detected. It is probable, that peaks C-C_1 and I-C_1 result from coelution of different isomers.

In general eight isomers of C_0-phenanthrene-/anthracenecarboxylic acids exist. Five of them are phenanthrenecarboxylic acids and three are anthracenecarboxylic acids. Coelution experiments with authentic standards of 9-anthracenecarboxylic acid and 4- and 9-phenanthrenecarboxylic acid, showed that only 9-phenanthrenecarboxylic acid was present. It is the second eluting C_0-phenanthrene-/anthracenecarboxylic acid. Among the four compounds not identified at least one must be either 1- or 2-anthracenecarboxylic acid. Besides 4-phenanthrenecarboxylic acid, which is not present, only three further phenanthrenecarboxylic acid isomers, 1-,2- and 3-phenanthrenecarboxylic acid exist. Compound D differs from the former four C_0-phenanthrene-/anthracenecarboxylic

acids due to a stronger m/z 177 (M^+-$COOCH_3$). The compound is characterised by a relative depletion with increasing maturity. The relatively high proportions of compounds B and C may indicate, that these two isomers are 2-phenanthrene- and 3-phenanthrenecarboxylic acid. This is based on the consideration, that they in analogy to 2- and 3-methylphenanthrene probably are the most stable isomers (pers. comm. H. Willsch, FZ-Jülich, Germany) and that 2- and 3-methylphenanthrene are the predominating methylphenanthrenes in the aromatic fraction. Especially compound B-C_0 in contrast to D-C_0 shows an increase with increasing maturity.

The samples where 1-naphthalenecarboxylic acid was highly abundant (Fig. 6.47) show relatively high proportions of the first eluting C_0-phenanthrene-/anthracenecarboxylic acid as well. Among the 12 C_1-phenanthrene-/anthracenecarboxylic acids compound H-C_1 shows a mass spectrum similar to that of compound D-C_0. Additionally compound H-C_1 shows a depletion in rel-

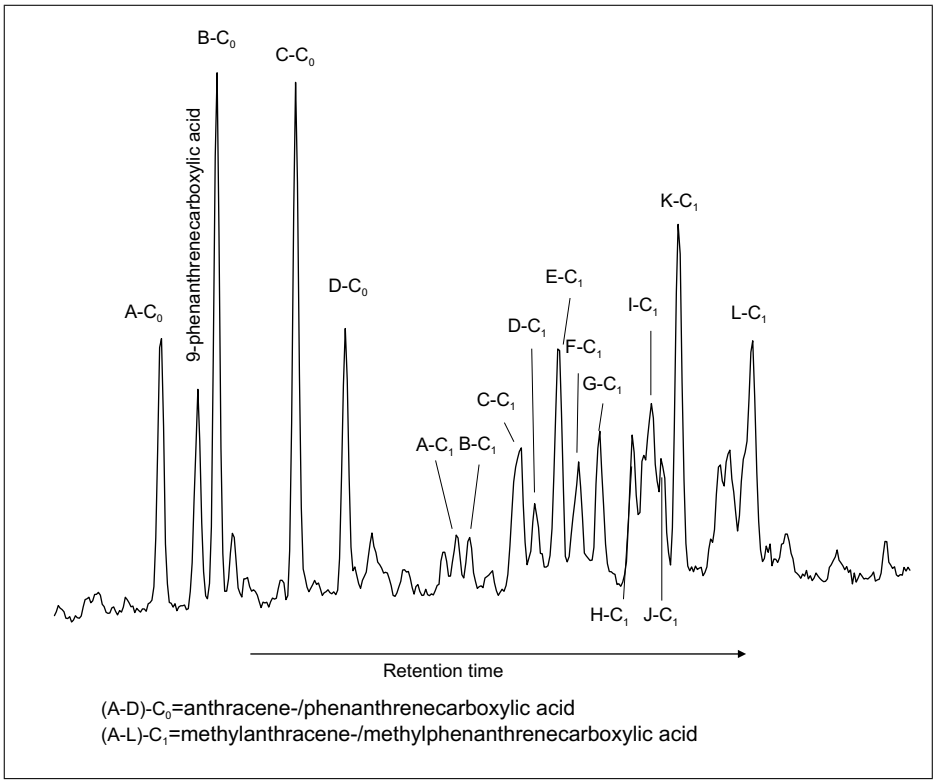

Figure 6.49: Gas Chromatogram displaying the distribution of $C_{(0-1)}$-phenanthrene-/anthracenecarboxylic acids (m/z 236, 250) in an Upper Carboniferous sample

ative amounts with increasing maturity, this strongly corresponding to the behaviour of compound D-C_1. It therefore is presumable that the two compounds are characterised by depleted thermal stabilities in comparison to other isomers.

Hopanoic Acids

Hopanoic acids ranging from C_{28} to C_{36} have been reported to occur in sediments (Bennett and Abbott, 1999). However normally C_{30-32} hopanoic acids are predominant in both sediments and oils (Bennett and Abbott, 1999; Meredith *et al.*, 2000). The compounds are formed via oxidation of the corresponding hopanes during microbial degradation of crude oils (Wantson *et al.*, 1999) and show a significant increase with increasing extent of biodegradation (Meredith *et al.*, 2000). This is contradictory to the studies of Behar and Albrecht (1984), wherein an apparent decrease in hopanoic acid concentrations with an increasing degree of biodegradation amongst five unrelated oils has been observed. On the other hand it has been suggested, that hopanoic acids may be potential precursors of hopanes (Bennett and Abbott, 1999). The authors observed an increase of hopanes accompanied by a decrease of hopanoic acids. Nevertheless they also point out, that hopanoic acids might be released from macromolecules with increasing maturity (Bennett and Abbott, 1999). Due to the fact that hopanoic acids and hopanes probably originate from the same precursors i.e. bacteriohopanetetrol and related biohopanoids, they are characterised by identical biogenic configuration, the 17β/21β(22R)-configuration (Rohmer *et al.*, 1992). This configuration is the least stable, and is converted into β/α- and α/β-isomers during diagenesis (Seifert, 1975). Additionally the 22R-isomers are transformed to the corresponding 22S-hopanoic acids resulting in an equilibrium mixture. This behaviour corresponds to the one of hopanes and the maturity profiles of the homohopanes and hopanoic acids has indeed been shown to be comparable (Bennett and Abbott, 1999).

Hopanoic acids were identified according to their mass spectra and literature. They were present in the range from C_{30} to C_{32}. Whereas most of the samples show the presence of six isomers, this does not account for the four coals from the Moscow Basin. These samples, in correspondence to the variety of hopanes also

show a high variability in hopanoic acids. C_{30}- and β/α-*S*- and -*R*-isomers of the C_{32}-hopanoic acids were only present in these samples. In contrast hopanoic acids present in the majority of the samples are the α/β- and β/α-*R* and *S*-isomers of the C_{31}-hopanoic acids and the α/β-*S*- and -*R*-isomers of the C_{32}-hopanoic acids. These samples showing maturities between 0.59 to 0.94% R_r are characterised by a clear predominance of α/β-(R) and (S) C_{31}-hopanoic acids over their β/α-(*R*) and (*S*)-counterparts. This is not observed for the more immature samples. They in general show a clear predominance of (*R*)- over (*S*)-isomers. Although this composition probably can be attributed to the relatively low thermal maturity, β/β-hopanoic acids were also absent in these samples, except for one β/β-C_{32}-hopanoic acid.

Resumée

n-Fatty acids are the predominant compounds of the acid fractions. They are present in all of the investigated samples. The majority of these samples shows a clear predominance of short-chain *n*-fatty acids, indicating that cuticular waxes of higher plants have been minor contributors to the organic matter. However the strong EOP for most of the samples indicates that alteration of *n*-fatty acid composition has been weak.

The distribution of aromatic carboxylic acids varies more widely. Benzoic acids, hydroxy- and methoxybenzoic acids are present in a wide maturity range. The composition of both C_{0-2}-benzoic acids and hydroxybenzoic acids shows a dependence on maturity. The presence of 4-hydroxy-3-methoxybenzoic acid and 3,4-dimethoxybenzoic acid indicates that gymnospermous lignin may contribute to the organic matter of the investigated samples. The absence of dehydroabietic acid in the Permian sample from South China corresponds to the fact, that diterpenes of the abietane type are predominantly present in sediments of the northern hemisphere.

The presence of alkylnaphthalenecarboxylic acids, alkylnaphthalenedicarboxylic acids and alkylphenanthrene-/-anthracenecarboxylic acids normally is restricted to samples of enhanced maturities. This strongly indicates, that these compounds

are formed at elevated temperatures. However, the presence of especially alkylnaphthalenedicarboxylic acids in some immature samples indicates, that the compounds may originate from two different sources and that only one depends on thermal maturity of organic matter. Hopanoic carboxylic acids were present in the majority of the samples. While normally only six isomers were present, the immature samples are characterised by a greater variety of these compounds.

7 Discussion

The broad geochemical investigations on forty Paleozoic samples are predominantly focussed on the biogenic significance of individual molecular compounds and compound classes. Biogenic compounds often are characterised by low thermodynamic stabilities and therefore in sediments are not preserved in their original structure. Modifications of the structure often make the assignation of the biogenic origin more difficult. A biogenic significance is indicated when the relative amounts of a compound do not strongly correlate to the amounts of corresponding isomers showing a similar thermodynamic stability. This means that due to the contribution from a specific source, the relative amounts of a biogenic compound often do not strongly represent the relationship between its thermodynamic stability and the thermal maturity of organic matter. Different compounds characterised by this and additionally showing a strong correlation often are characterised by a biogenic relationship.

The composition of organic matter besides its origin is influenced by its thermal maturity and depositional environment. Biogenic relationships of individual compounds are often more apparent for organic matter of low thermal maturity. Over a wide maturity range both depositional environment and sources of organic matter i.e. terrestrial or marine normally are recognisable. When discussing the biogenic significance of individual compounds and compound classes this background therefore has to be considered first. As a byproduct of this thesis focussing on biogenic relationships, the origin and formation pathway of compounds and compound classes that show no strong biogenic significance will also be considered.

For the discussion the investigated samples have been separated into four groups. The North English coals represent the biggest group (Group I), characterised by

a moderate maturity range. This group is supposed to give a common overview over the potential biogenic relationships of individual compounds and compound classes. The second group (Group II) represents immature coals from different locations. Correlations within this group are supposed to support the potential biogenic relationships indicated by the composition of the North English coals. Additionally biogenic relationships which are not obvious within the maturity range of the North English coals may be recognisable due to this subset. The third group (Group III) consists of samples characterised by elevated thermal maturities and strongly varying depositional environments. This group probably is of less relevance with respect to the biogenic significance of individual compounds and compound classes but strongly represents both the influence of depositional environment and thermal maturity on organic matter. The last group (Group IV) in contrast to the three previous groups covers samples characterised by enhanced proportions of type I kerogen, most of them being immature. This group therefore helps to assess the terrestrial significance of individual compounds and compound classes. Additionally the immaturity of this group and group II may help to assess compounds which are typical for immature organic matter independently to its origin.

Prior to the discussion on the origin of the compounds and compound classes a broad characterisation of the thermal maturity and the environmental factors for all investigated samples will be carried out. Although this will not be considered for the biogenic and non-biogenic significance in general it is necessary to prevent misinterpretations. For the investigations molecular compounds and compound classes of five fractions were considered. For the discussion of biogenic relationships two of them, aliphatic hydrocarbons and medium-polarity NSO compounds often are not respected. For the samples investigated in this study, the composition of aliphatic hydrocarbons does not indicate biogenic relationships but depositional environments and thermal maturities of organic matter. Medium-polarity NSO compounds in contrast have been rare for the majority of the investigated samples and interpretations due to this are vague.

For compounds and compound classes revealing a biogenic significance finally the chemotaxonomy of modern land plants will be considered.

7.1 Maturity assessment and determination of environmental factors influencing the samples

7.1.1 North English Coals, Group I

The subset of North English coals consists of 20 samples originating from six drilling locations. The age of the samples expands from Namurian to Westphalian C, normally consisting of a mixture of type II-III kerogen (Fig. 7.1 B). The samples with two exceptions, are characterised by relatively small variations of T_{max} and a more variable but still narrow range of vitrinite reflectances (0.67-0.94% R_r) (Fig. 7.1 A). The two coals from Rowlands Gill show relatively high vitrinite reflectances (1.23-1.26% R_r), corresponding to an enhanced T_{max} (Fig. 7.1 A). Although T_{max} values (431-438°C) respecting the vitrinite reflectances are consistently lower than many published data (Epistalié and Bordenave, 1992) they correspond to the ones reported by Littke *et al.* (1990). The authors suggested lower T_{max} values to be characteristic for coals. However the low T_{max} for one sample from Potato Pot (Fig. 7.1 B) strongly contradicts its vitrinite reflectance (Tab. 5.1). Due to the lack of sample material Rock-Eval pyrolysis was not carried out a second time. It is assumed, that the low T_{max} is erratic. Contamination is improbable as molecular geochemical results are in good agreement with the ones for the two other coals from Potato Pot, which do not refer to contamination. Plots of T_{max} therefore do not respect this specific sample (Fig. 7.2).

Due to the relatively high proportions of vitrinite for all of the North English coals (Table A.1), vitrinite reflectances and T_{max} were expected to show good correlation. However this is not generally true (Fig. 7.1 A). While the majority of the samples show strong correlation, few are characterised by enhanced deviations from average distributions (Fig. 7.1 A). Respecting the procedures for estimating both R_r and T_{max} it is assumable, that scattering represents the different influences of the individual sample composition on T_{max}. This is well-founded by the fact, that R_r does only depend on the presence of vitrinite, while T_{max} is influenced by the complete petrographic composition of a sample.

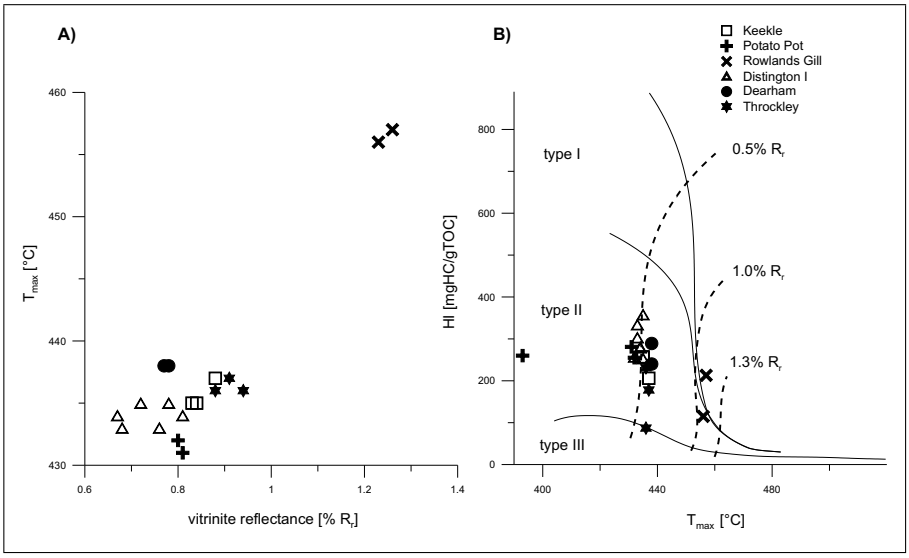

Figure 7.1: Cross plots of A) T_{max} *vs.* vitrinite reflectance and B) HI *vs.* T_{max} for North English coal samples

Normally neither T_{max} nor HI of the North English coals correspond to type I kerogen (Fig. 7.1 B). T_{max} for type II and III kerogen on the other hand does not differ significantly. Normally values are only slightly lower for the latter type. Nevertheless small deviations which are observed for individual samples may result from different composition in organic matter. However, it is unlikely that more pronounced scattering can be explained by differences in kerogen typing due to the similarity of T_{max} for type II and III kerogen.

Strongest deviations are observed for the two coals from Dearham, characterised by a relatively high T_{max} and the two samples originating from Potato Pot showing comparably low ones (Fig. 7.1 A). All four samples at least show a strongly different composition in maceral groups (Table A.1). Nevertheless T_{max} is characterised by a strong dependence on the individual locations while organic matter composition seems to be of little importance.

Two distinct factors that are known to influence T_{max} are the amounts of resinite in a sample (Peters, 1986) and its mineral matrix (Katz, 1983; Littke, 1993). While the presence of resinites can strongly reduce T_{max}, high amounts of specific minerals, to different extends result in an enhanced T_{max} due to adsorption of organic matter on the mineral surfaces (Littke, 1993). Both effects are not recognisable

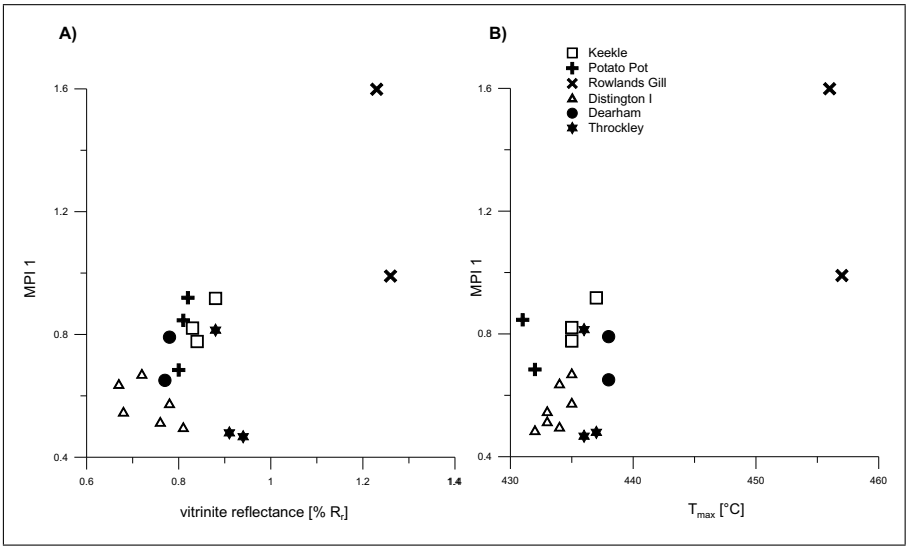

Figure 7.2: Cross plots of A) MPI-1 *vs.* vitrinite reflectance and B) MPI-1 *vs.* T_{max} for North English coal samples

for the North English coals. The mineral matrix effect is known to be negligible for samples showing high amounts of organic matter (Katz, 1983; Langford and Blanc-Valleron, 1990). The influence of the mineral matrix, if present should be recognisable for samples that show relative high amounts of minerals only. This is true for two samples originating from Throckley and one from Rowlands Gill, which show low amounts of TOC (Table A.1). However none of them is characterised by a significantly enhanced T_{max}. Therefore it can be presumed, that the mineral matrix of the North English coals shows no significant influence on T_{max}. The influence of resinites for T_{max} can not be estimated directly. The relative proportions of compounds originating from resinous sources (cadalene, retene, ip-iHMN) however, show no distribution that would support a significant influence of resinites on T_{max}. For the North English coals vitrinite reflectance in comparison to T_{max} will be considered as the more reliable maturity parameter.

Regarding to their vitrinite reflectances higher than 0.6% R_r, all North English coals are expected to have passed diagenesis and to some extend have suffered catagenetic transformations. Aliphatic hydrocarbons mainly are influenced by processes that are restricted to the diagenetic stage. Therefore their composition maintained little information for the classification of the English samples. In fact hopane ratios have reached equilibrium (Fig. 6.7); in correspondence to literature

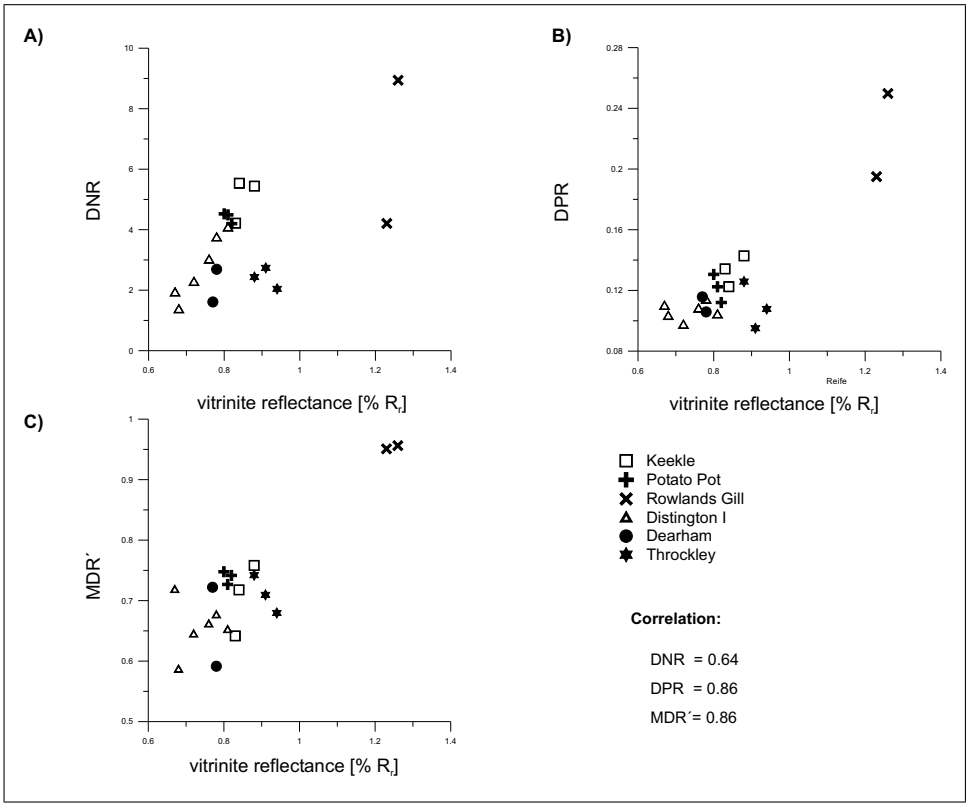

Figure 7.3: Cross plots of A) DNR, B) DPR and C) MDR' *vs.* vitrinite reflectance for North English coal samples; for definition of the used maturity parameters see Tables 6.4, 6.6 and 6.7

(Radke *et al.*, 1980; Littke *et al.*, 1990; Norgate *et al.*, 1999), all samples are characterised by CPI values not significantly higher than one (Table 6.1).

Maturity parameters based on aromatic hydrocarbons, in contrast are not restricted to low maturity levels. Among several established parameters (Radke *et al.*, 1982b, 1986; Alexander *et al.*, 1986b), the MPI-1 (Table 6.6) is generally accepted to strongly correspond to maturity for organic matter predominantly originating from terrestrial sources and showing maturities beyond 0.6% R_r.

Although MPI-1 is not the molecular parameter showing strongest correlation to maturity, it indeed corresponds to vitrinite reflectance for the majority of the North English coals (Fig. 7.2 A). The most striking deviations are given for the Namurian coal from Rowlands Gill and two samples from Throckley. These three samples are characterised by low TOC contents. The strong deviation for the sample from Rowlands Gill can be attributed to its organic matter composition,

which might also explain the scattering of samples from Distington (Fig. 7.1 B). The low MPI-1 values of the two samples from Throckley indicate, that these samples differ strongly from the rest of the North English coals. This can not be attributed to the kerogen typing (Fig. 7.1 B) and therefore may result from either depleted isomerisation reactions due to a weaker mobile phase or due to another sedimentological history. It for example may be possible that the Throckley borehole has been subject to a fast heating rate which did not affect the mobile phase that strong.

A comparison between the MPI-1 *vs.* vitrinite reflectance and MPI-1 *vs.* T_{max} plots (Fig. 7.2 A and B) shows that especially for the coals from Dearham and Potato Pot, vitrinite reflectance is a more reliable parameter than T_{max}. In Fig. 7.2 B deviations again are strong for two of the three samples from Throckley and the Namurian coal from Rowlands Gill. In contrast this does not account for the sample subset originating from Distington. Actually MPI-1 and T_{max} are characterised by a good correlation for coals from Distington, while for the correlation between MPI-1 and vitrinite reflectance they show a random distribution (Fig. 7.2 A and B).

Besides the MPI-1 many maturity parameters based on aromatic hydrocarbons do also reveal good accordance to vitrinite reflectances (Fig. 7.3 A-C). The correlation for individual sample subsets are variable, while especially the coals from Throckley normally show strong deviations (Fig. 7.3). The samples from Potato Pot are characterised by the strongest similarity. This again supports the unreliability of the low T_{max} for one of these coals. Samples from Keekle show a more or less pronounced correlation to the maturity parameters, without strong scattering. Both Keekle and Potato Pot are located in the West Cumbrian Coalfield and the analogy in behaviour accords to a similar sedimentological history. Amongst samples from Distington deviations normally are strongest for the two samples of highest and lowest vitrinite reflectance (Fig. 7.3 A-C), while especially the DNR strongly correlates to the maturity for this subset of samples. This indicates that the composition of alkylnaphthalenes for the samples from Distington does not depend on the origin of organic matter but on the thermal maturity. The effect of different kerogen typing despite their enhanced maturity is recognisable

for the two coals from Rowlands Gill. This is indicated by the strongly different behaviour especially in DNR and DPR (Fig. 7.3 A-B). In contrast, the two coals from Dearham do only show a similarity for ratios of alkylphenanthrenes, this contradicting their kerogen typing based on the HI (Fig. 7.3, 7.1 B).

The majority of the ratios therefore based on the vitrinite reflectance helps to assess the maturity of individual samples, while deviations indicate, that distinct effects like contribution from a specific source or depositional environment are still recognisable within the investigated maturity range.

The HI *vs.* T_{max} plot (Fig. 7.1 B) serves to classify the composition of organic matter and to explain deviations observed within the maturity assessment for the North English coals. With regard to the narrow range of T_{max} for most of the North English samples, they all are characterised by equal maturities in the HI *vs.* T_{max} plot (Fig. 7.1 B). The two coals from Rowlands Gill again differ significantly due to their enhanced maturity (Fig. 7.1). Although all North English coals, with two exceptions, predominantly consist of a mixture of type II-III kerogen, they nevertheless are characterised by some differences.

The Namurian sample from Rowlands Gill corresponds to type I kerogen, explaining the strong deviations for the MPI-1 (Fig. 7.1 B, Fig. 7.2 A and B). In contrast the scattering of samples from Distington does not strongly correspond to HI. However samples from Distington sometimes are characterised by elevated HI with respect to the rest of the North English coals.

Considering HI, the three coals from Potato Pot represent a uniform subset of samples (Fig. 7.1 B). Their vitrinite reflectances and HI values do not differ significantly. The three samples from Keekle, which are characterised by a wider maturity range (0.83-0.88% R_r) show a more pronounced variability in HI corresponding to the vitrinite reflectances. The sample of lowest HI is characterised by the highest maturity (Fig. 7.1). HI for the two coals from Dearham in contrast to the T_{max} *vs.* vitrinite reflectance plot (Fig. 7.1 A) is characterised by a good correlation to the HI for coals from Potato Pot. The samples from Throckley and Distington, in correspondence to Fig. 7.1 A are characterised by a wider scattering in HI. HI values for the three samples from Throckley vary significantly and do

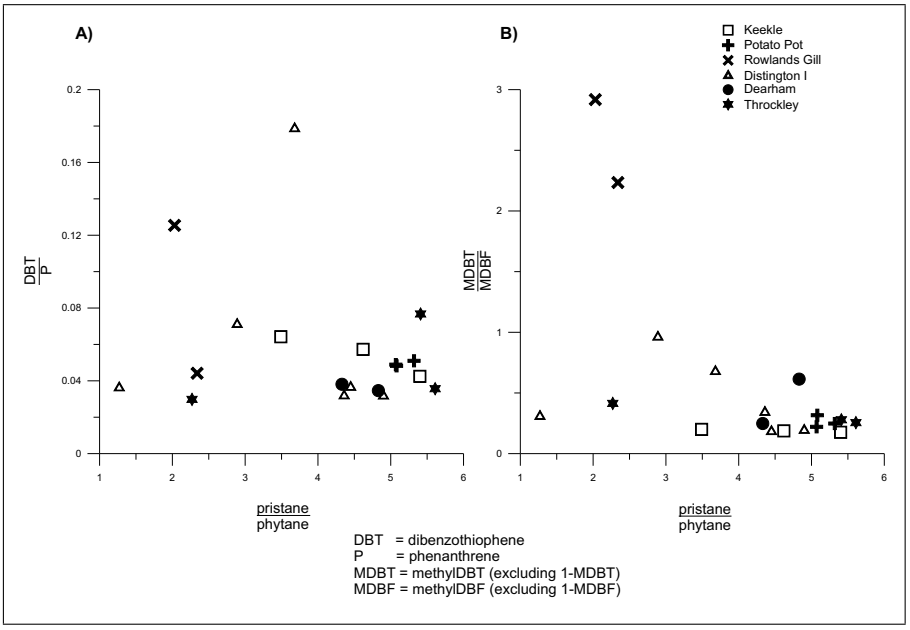

Figure 7.4: Cross plots of A) DBT/P and B) MDBT/MDBF *vs.* the ratio of pristane/phytane for North English coal samples

not correspond to their T_{max} but to their vitrinite reflectances. The kerogen of the most mature sample from Throckley may be classified as type III (Fig. 7.1 B). Due to T_{max} for the Throckley samples not referring to an influence of minerals this is also improbable for HI. Nevertheless the strong differences for these samples are left unexplained and do not correspond to the strong deviations for the majority of the maturity parameters (Fig. 7.2, 7.3). Although the samples from Distington show strong variations for HI (Fig. 7.1), this does not hold for the scattering in maturity parameters. The fact, that vitrinite reflectances do not correspond to T_{max} and HI indicates, that the samples from Distington are characterised by enhanced variations in kerogen composition. However three samples representing highest HI of the complete English sample set are not the ones showing strongest deviations for maturity parameters.

Molecular geochemical parameters representing depositional conditions in contrast to maturity parameters are rare. The absence of gammercerane and C_{35}-hopanes however indicates that depositional environments for North English coals have not been hypersaline. While C_{29}-steranes indicate a contribution of organic matter from higher plants, they have only been present as minor compounds in few of

the North English samples and therefore possess little significance. Nevertheless especially the scattering of samples from Distington for many maturity parameters corresponds to their inhomogeneities in the few parameters representing depositional environment. This does account for the ratios of pristane/phytane, pristane/$n-C_{17}$ and alkyldibenzothiophenes to both alkylphenanthrenes and alkyldibenzofurans. These parameters for some samples from Distington often differ from the relatively similar values for the rest of the North English coals. In correspondence to its kerogen typing the Namurian sample from Rowlands Gill is characterised by a relatively high CPI_{HC} of 1.27 (Table 6.1), an enhanced ATR_{HC} and low ratios of pristane/phytane and pristane/$n-C_{17}$ (Table 6.2). These values strongly correspond to the kerogen typing and the strong deviation for the MPI-1 (Fig. 7.2). The majority of the North English samples show high pristane/phytane and pristane/$n-C_{17}$ ratios (Table 6.2), which does not account for the Distington samples in general. While the behaviour of aliphatic hydrocarbons does only show strong deviations for two samples from Distington, amounts of alkyldibenzothiophenes to alkyldibenzofurans and -phenanthrenes correspond to the deviating behaviour of two further coals from Distington. Generally enhanced proportions of alkyldibenzothiophenes are attributed to organic matter originating from marine sources. Although alkyldibenzothiophenes were generally present in minor amounts, two samples from Distington show a relative enrichment of these compounds, but lowest vitrinite reflectances (Fig. 7.4). This supports the hypothesis that these samples are characterised by relative high amounts of organic matter, not originating from terrestrial sources and therefore may explain deviations in maturity parameters especially for the MPI-1. The relatively high proportions of alkyldibenzothiophenes for the two samples from Rowlands Gill (Fig. 7.4) correspond to their comparably high proportions of organic sulphur (Table A.1). They may also result from progressive maturation of organic matter.

Altogether, differences in depositional environment and sources of organic matter but probably also geological age are recognisable in both bulk and molecular geochemical parameters. The samples from Keekle and Potato Pot, all of Westphalian age represent relatively homogenous subsets. The two coals from Dearham are characterised by a similar behaviour to the Potato Pot samples. Nevertheless organic matter composition among these two samples differs more significantly than

for the ones from Keekle and Potato Pot. The Dearham coals were deposited during the Namurian. The two coals from Rowlands Gill are characterised by significantly enhanced maturities. Additionally the Namurian coal from Rowlands Gill is the one of the whole set, which mostly represents type I kerogen. This characteristic, despite its enhanced maturity is still recognisable for some of the maturity parameters based on aromatic hydrocarbons (Fig. 7.2, 7.3). The differences for samples from Distington can be attributed to their different organic matter composition, predominantly represented by the ratios of dibenzothiophene/phenanthrene and methyldibenzothiophenes/methyldibenzofurans (Fig. 7.4). The Distington samples belong to the Westphalian and Namurian. The Namurian is characterised by marine transgressions corresponding to a more or less terrestrial signature of the organic matter. The variations of the Throckley coals in contrast do not correspond to differences in organic matter composition. The behaviour of this subset of samples can not unambiguously be explained by factors like depositional environment or organic matter composition and may despite the T_{max} values correspond to influences of the mineral matrix or a fast heating period on the organic matter.

7.1.2 Immature Type III Coals, Group II

Six samples, two from Germany and the Moscow Basin respectively and one from South China and Spitsbergen, equally to the North English samples, are also characterised as coals consisting predominantly of mixed type II-III kerogen (Fig. 7.5 B). The age of these coals extends from Upper Viséan to Permian. In contrast to the North English coals, they are, with two exceptions, characterised by lower vitrinite reflectances normally corresponding to depleted values of T_{max} (Fig. 7.5 A). Additionally variations in T_{max} are much more pronounced than for the North English coals. This corresponds to literature (Epistalié and Bordenave, 1992), reporting that T_{max} normally shows a stronger increase in comparison to vitrinite reflectances. However, the two samples from Germany are characterised by the same vitrinite reflectance but strong differences in T_{max} (Fig. 7.5 A). Additionally the coal from South China shows an elevated T_{max}. Differences in kerogen typing (Fig. 7.5 B) for the two more mature samples from South China and Spitsbergen are not strong enough to hold for the differences in T_{max}. Actually the amounts of resins may have an influence on the behaviour of the South Chinese coal as it is the only one of this subset of samples, which is characterised by the absence of dehydroabietic acid, an important constituent of resins. This may indicate, that the amounts of resins are significantly depleted for this coal not originating from the Euramerian flora realm. Whether the differences for the two German coals can also be attributed to the contents of resins is insecure. Surely they do not result from mineral matrix effects, as both coals show high TOC contents (Table A.1). The two coals are characterised by differences in kerogen composition. However, the enhanced T_{max} for the Upper Viséan coal contradicts its HI, strongly corresponding to type III kerogen (Fig. 7.5 B).

The differences in kerogen typing for the two German samples correspond to the differences for the two coals originating from the Moscow Basin. While one of the coals for each location is characterised by enhanced proportions of type III organic matter, the second shows a kerogen composition similar to the ones of the North English coals (Fig. 7.5 B). However, in contrast to the German coals, T_{max} does not differ strongly for the two coals originating from the Moscow Basin. Except for the two coals showing enhanced correlation to type III organic matter,

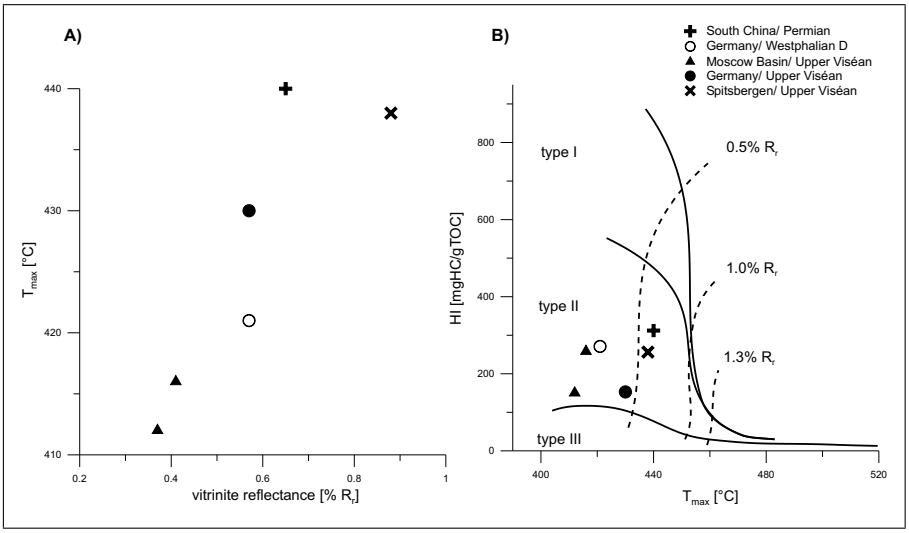

Figure 7.5: Cross plots of A) T_{max} *vs.* vitrinite reflectance and B) HI *vs.* T_{max} for type III coals from different locations and ages

the other coals are characterised by a composition corresponding to the one of the North English coals.

Due to the relatively low maturity of the six coals, maturity parameters based on aliphatic hydrocarbons are expected to strongly correspond to maturity. In contrast maturity parameters of aromatic hydrocarbons will show little correlation at least for the coals from Germany and the Moscow Basin. Indeed ratios representing the distribution of 22*S*- to 22*S*- and 22*R*-17α(H),21β(H)-29-dihomohopanes strongly correspond to vitrinite reflectance (Fig. 7.6 A). For the more mature sample from the Moscow Basin the ratios could not be determined due to negligible amounts of hopanes. Equilibrium is reached for the two more mature coals from Spitsbergen and South China (Fig. 7.6 A). The two coals from Germany show ratios contradicting their T_{max}. Considering the ratio of dihomohopanes the Westphalian D sample is supposed to show a higher maturity (Fig. 7.6 A). The relative amounts of hopanes to moretanes are of little significance. Except for the one coal from the Moscow Basin all other coals have reached equilibrium (Fi. 7.6 B). In contrast to CPI_{HC} for the North English coals, samples of maturities below 0.6% R_r, with one exception are characterised by values strongly differing from one (Fig. 7.6 C), this corresponding to literature (Radke *et al.*, 1980; Norgate *et al.*, 1999). The low CPI_{HC} for one of the samples originating from the Moscow Basin

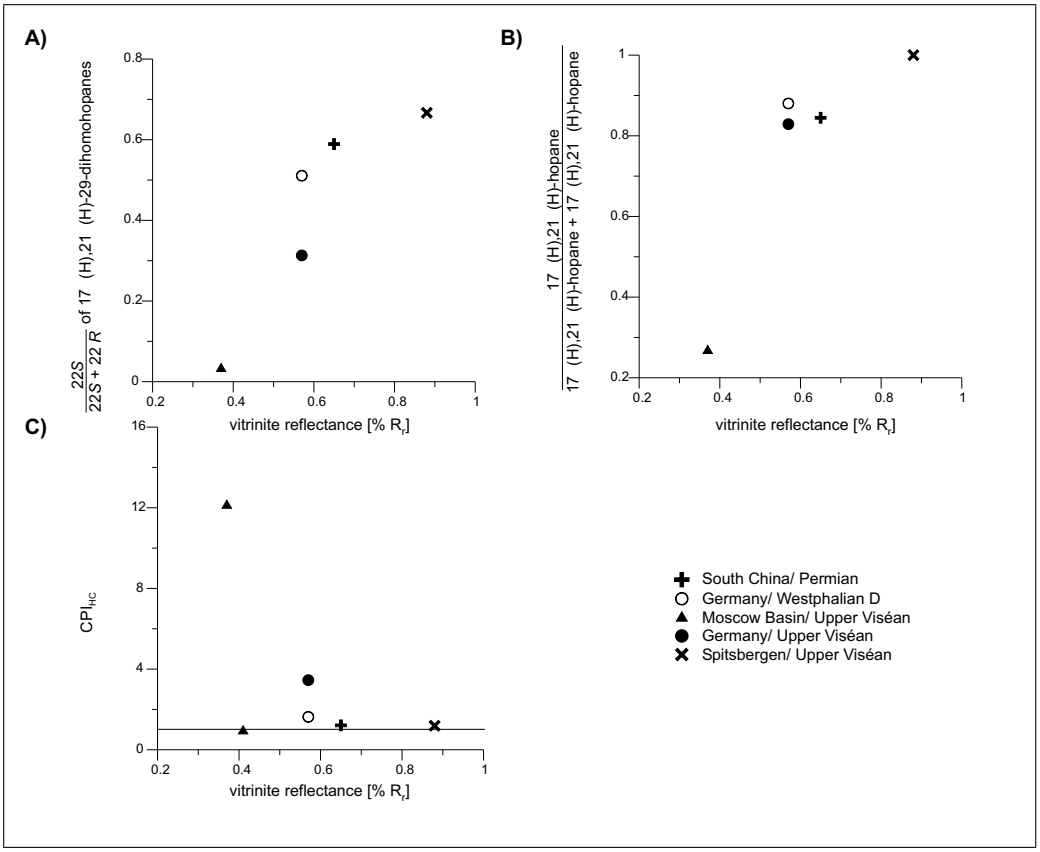

Figure 7.6: Cross plots of A) $22S/22S$- + R of 17α(H),21β(H)-29-dihomohopane, B) C_{32}-(17α(H),21β(H)-/17α(H),21β(H)- + 17β(H),21α(H))-hopane and C) CPI_{HC} *vs.* vitrinite reflectance

can be attributed to the fact, that its organic matter has been deposited under reducing conditions. Even over odd (EOP) predominance of *n*-alkanes in reducing environments is suggested to result from the reduction of the corresponding even-numbered *n*-fatty acids (Lutz *et al.*, 2000). The second sample from the Moscow Basin in contrast is characterised by a significantly enhanced CPI_{HC}. Additionally this sample shows the presence of $\beta\beta$-homologues and of hop-17(21)-enes and significantly depleted values for the hopane ratios (Table A.14, A.16). $\beta\beta$-Hopanes are absent at maturities beyond 0.4% R_r (Peters and Moldowan, 1993) and their presence indicates that the sample has been altered little by thermal influence.

Maturity parameters of aromatic hydrocarbons, except for the MPI-1 and -2 showed no correlation to the vitrinite reflectance of the six type III coals. The

good correlation of the MPIs for the samples can be attributed to the fact, that their organic matter predominantly originates from terrestrial sources.

According to kerogen typing the six coals are supposed to contain organic matter predominantly derived from terrestrial sources. However their ratios of pristane/phytane vary significantly (Table 6.2). The highest value amongst all investigated samples is the one of the coal from South China, indicating that it has been deposited under strongly oxidising conditions. The values for coals from Germany and Spitsbergen are low in comparison to that of the South China coal but nevertheless indicate a deposition of terrigenous organic matter under oxidising conditions. Additionally the two German coals, contrary to their differences in kerogen composition, amongst all samples where steranes have been present in quantifiable amounts, are characterised by sterane distributions indicating a strong contribution of organic matter from terrestrial sources (Fig. 6.5). The two coals from the Moscow Basin in contrast to the rest of the low maturity coals, show values of pristane/phytane significantly lower than one (Table 6.2), indicating anoxic depositional environments. Composition of organic matter however due to pristane/$n-C_{17}$ values strongly differs for the two samples. The sample characterised by a low CPI_{HC}, higher maturity and less pronounced kerogen III typing shows a value indicating a stronger input of organic matter from terrestrial sources. The value may also indicate enhanced biodegradation. For the two samples it generally can be assumed, that although they have suffered little thermal alteration, they were affected by diagenetic processes to different degrees. The less mature coal probably contains higher amounts of organic matter originating from non terrestrial sources, while due to its ATR_{HC} terrestrial contribution is still recognisable. The presence of hop-17(21)-enes may not only indicate low thermal alteration but also different depositional conditions. The other sample in contrast is characterised by stronger contribution of organic matter from terrestrial sources, while either conditions of deposition have been more anoxic or the sample has been subject to enhanced biodegradation. Due to the relative low amounts of aliphatic hydrocarbons and elevated proportions of aromatic hydrocarbons biodegradation is more probable.

Alkyldibenzothiophenes were absent in this coal. Besides this sample alkyldibenzothiophenes were also absent in the two coals from Germany. This indicates a strong terrigenous character of organic matter. Generally proportions of alkyldibenzothiophenes were also low for the other samples, indicating a fluvio/deltaic depositional environment (Fig. 6.24, 6.29).

7.1.3 Samples Containing Type II-III Kerogen of Enhanced Thermal Maturities, Group III

Seven samples have been investigated, also consisting predominantly of type II-III kerogen (Fig. 7.7 B), but showing relative enhanced vitrinite reflectances in comparison to the previously discussed samples. This subset of sample consists of two fossils from the Upper Carboniferous, four Upper Permian sediments from East Greenland and a coal originating from a Permian deposit in Russia. In contrast to the previously discussed samples correlation between vitrinite reflectance and T_{max} is weak (Fig. 7.1 A). The *Mesocalamites cf. Taitianus* in agreement with its significantly enhanced vitrinite reflectance is characterised by a strongly elevated T_{max}. The scattering of the other samples results from depleted values of T_{max} for the more mature samples from East Greenland, the significantly enhanced value for one from the less mature samples of this location and the weak correlation between the *Sigillaria* and the Permian coal.

The significantly enhanced T_{max} for one sample from East Greenland clearly can be attributed to a mineral matrix effect resulting in a strong adsorption of lean organic matter (Table A.1) on minerals (Langford and Blanc-Valleron, 1990). De-

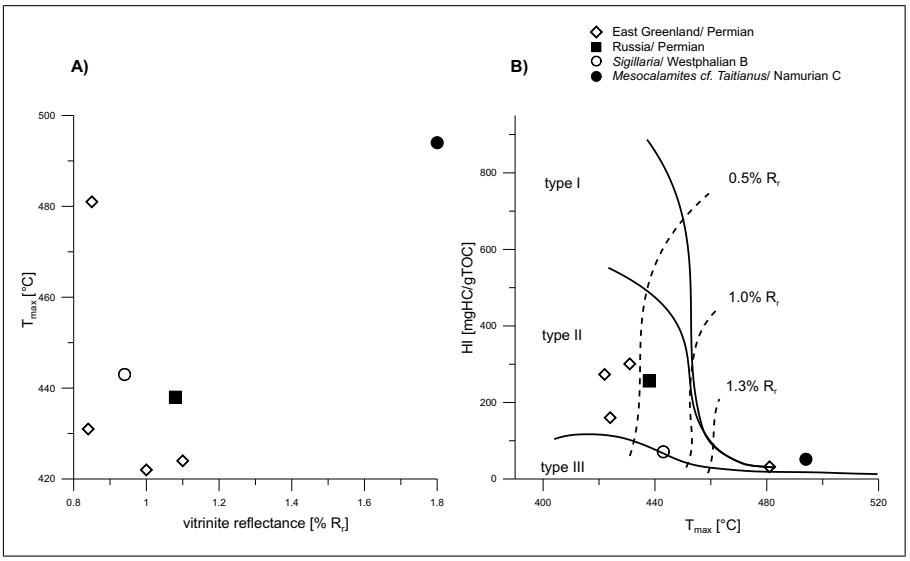

Figure 7.7: Cross plots of A) T_{max} *vs.* vitrinite reflectance and B) HI *vs.* T_{max} for type II-III kerogen samples of enhanced maturity

viations for the rest of the samples from this subset are difficult to assign due to their strong differences in composition (coal, fossils, sediments). However, in comparison to the North English coals, three samples from East Greenland are characterised by significantly depleted T_{max}, while the one for the Permian coal is also lower than would be expected due to its vitrinite reflectance (Table A.2). This for the Russian coal corresponds to the former mentioned suggestions of Littke *et al.* (1990), that lower T_{max} values are characteristic for coals. The low values for the samples from East Greenland, with one exception, indicate that despite their low TOC, Rock Eval data is not influenced by a mineral matrix effect.

In accordance with their enhanced maturities, hopane ratios have reached equilibrium values (Fig. 6.7), except for one sample from East Greenland. Maturity parameters of aromatic hydrocarbons especially based on alkylphenanthrenes show a stronger correlation to vitrinite reflectance than to T_{max}. Although, indicating that vitrinite reflectance is the better maturity parameter, this is less pronounced than for the previously discussed subsets. However, correlation of individual isomers especially for alkylnaphthalenes is better for T_{max}. In accordance to the hopane ratio, the one sample from East Greenland normally is characterised by depleted values of maturity parameters (Fig. 7.8). This contrary to the Throckley samples, which have also often been characterised by depleted values (Fig. 7.3) may be due to the high contents of minerals. Regarding Salmon *et al.* (1997, 2000), a sorptive protection mechanism may account for the relative low maturity of extractable organic matter. However, a confirmation would need further investigations on the mineral composition of the sample.

The ratios for the *Mesocalamites cf. Taitianus* strongly influence the correlation due to the significantly enhanced maturity (Fig. 7.8 A). When the sample is excluded correlations of ratios to vitrinite reflectance are much more pronounced for alkylnaphthalenes (Fig. 7.8 B and C) than for ratios based on alkylphenanthrenes and -dibenzothiophenes. This corresponds to the findings for the Distington samples, supporting the hypothesis that composition of alkylnaphthalenes is not significantly influenced by environmental factors. The maturity ratios for different compound classes show a better correlation to each other than to the vitrinite reflectance. This has already been observed for the North English coals. van Aarssen

et al. (2001) assumed, that maturity parameters may be influenced by different reaction environments to variable magnitudes. The correlation between different maturity parameters at enhanced maturities actually indicates, that these different reaction environments influence the composition of different compound classes in the mobile phase of individual samples to same extends while these influences do not necessarily correspond to the vitrinite reflectance.

The HI *vs.* T_{max} plot (Fig. 7.7 B) indicates, that the kerogen typing of the Permian sample from Russia and two from East Greenland is analogue to those of the North English coals. The two fossils however are characterised by a stronger correlation to type III kerogen (Fig. 7.7 B). In agreement with its elevated T_{max}, the sample characterised by a mineral matrix effect does also show a depleted HI (Fig. 7.7

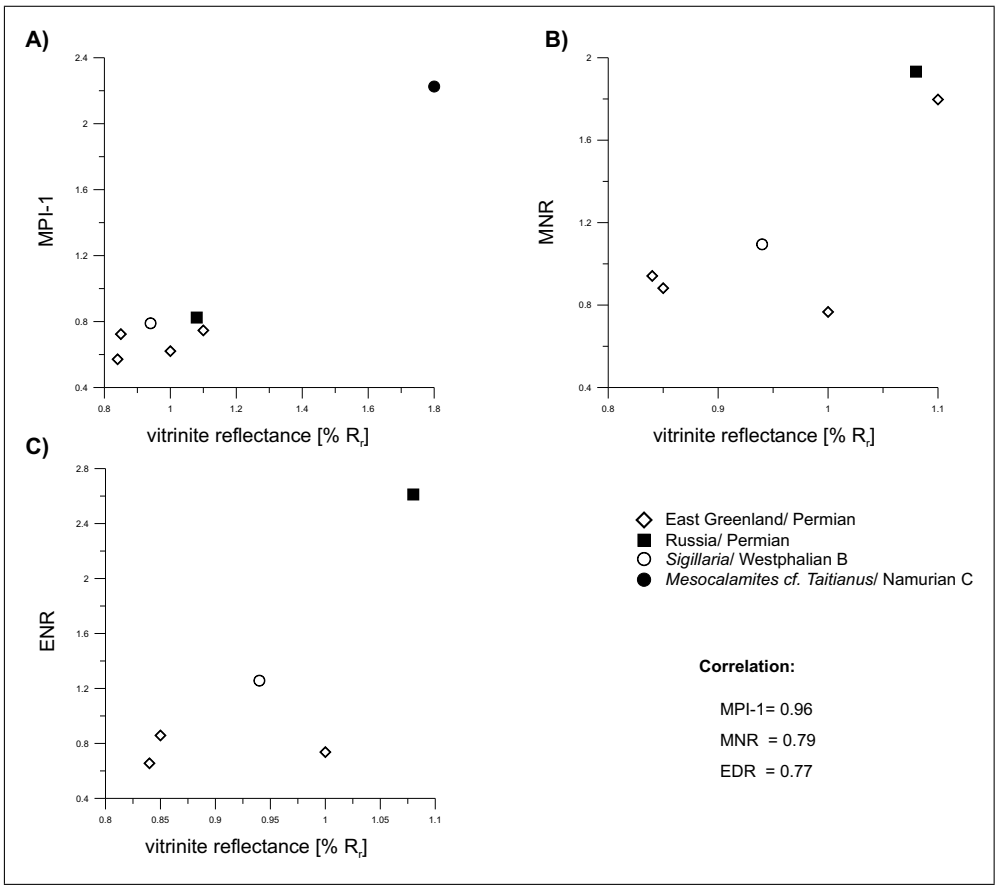

Figure 7.8: Cross plots of A) MPI-1 *vs.* vitrinite reflectance, B) MNR *vs.* vitrinite reflectance and C) ENR *vs.* vitrinite reflectance; for definition of the used maturity parameters see Tables 6.4 and 6.6

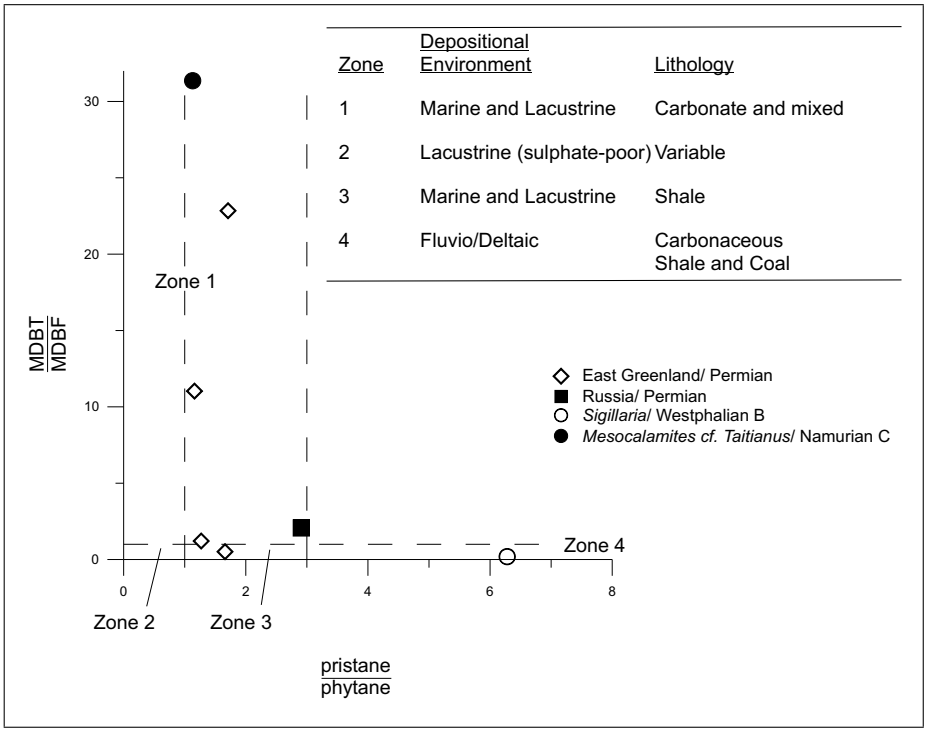

Figure 7.9: Cross plot of methyldibenzothiophenes/methyldibenzofurans *vs.* pristane/phytane

B). The sample where extractable organic matter may have been preserved via sorptive protection mechanisms shows high amounts of type III kerogen (Fig. 7.7 B).

According to the ratios of pristane/phytane and pristane/$n-C_{17}$ the samples are characterised by significant differences. Except for the *Sigillaria* and the Permian coal, none of them has been deposited under strongly oxidising conditions. However in correspondence to the kerogen typing they all are characterised by pristane/$n-C_{17}$ ratios supporting a strong contribution from terrestrial sources. While ratios of alkyldibenzothiophenes to -phenanthrenes assigns organic matter of all seven samples to have been predominantly deposited in lacustrine or fluvio deltaic environments (Fig. 6.24), the relative amounts of alkyldibenzofurans to alkyldibenzothiophenes indicate that some may have been deposited in marine environments (Fig. 7.9). Although probably not the main factor, it should be recognised, that maturity of North English coals has a significant influence on the proportions of alkyldibenzothiophenes. Therefore the relative high amounts

especially for the *Mesocalamites cf. Taitianus* are more significant according the maturity than the depositional environment. In general the relative enhanced maturity of the seven samples does not result in a more homogenous behaviour. This correlates to the differences in kerogen typing and composition in extractable organic matter for the two North English coals from Rowlands Gill. Whether recognised differences result from specific sources, different depositional environments or different degrees of protection however is insecure.

7.1.4 Samples Containing Predominantly Type I Kerogen, Group IV

Seven samples can not be assigned to type II or III kerogen. Three of them originate from the Permian in South France and although Rock-Eval pyrolysis has not been carried out, due to their geological background (pers. com. F. Körner), they are supposed to predominantly contain type I kerogen. Three samples originate from the Upper Viséan of the Moscow Basin; two of them are cannel-boghead coals. One sample originates from the Givetian or Frasnian of Spitsbergen and is a cannel coal.

Due to Rock-Eval pyrolysis carried out for four of the samples only, correlation between vitrinite reflectance and T_{max} (Fig. 7.10 A) is of little significance. Three of the four samples are characterised by small variations in vitrinite reflectance and therefore also in T_{max}. Considering the vitrinite reflectances, T_{max} values for the samples, in comparison to all type II-III samples are generally elevated. Actually the values are typical for immature samples of type I kerogen (Epistalié and Bordenave, 1992). Due to their low vitrinite reflectances, maturity parameters based on aliphatic hydrocarbons are significant for the immature samples from the Moscow Basin (Fig. 7.11). In contrast hopane ratios for the cannel coal from

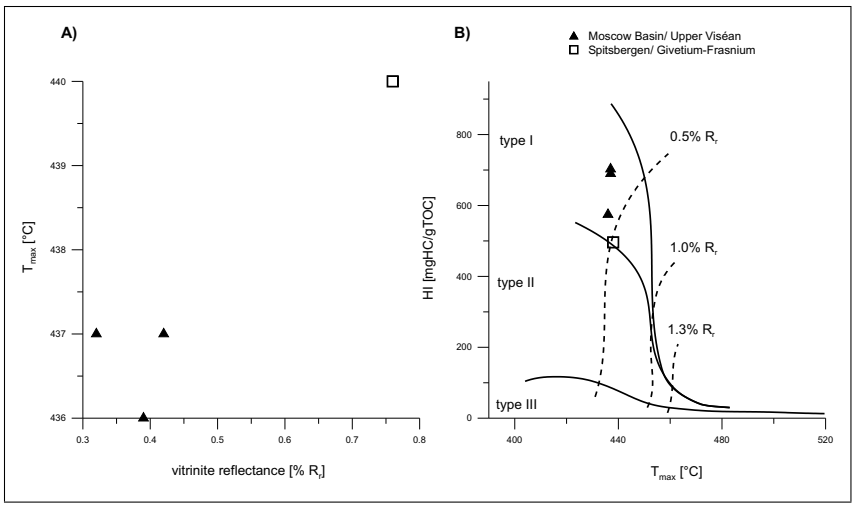

Figure 7.10: Cross plots of A) T_{max} *vs.* vitrinite reflectance and B) HI *vs.* T_{max} for type I kerogen samples

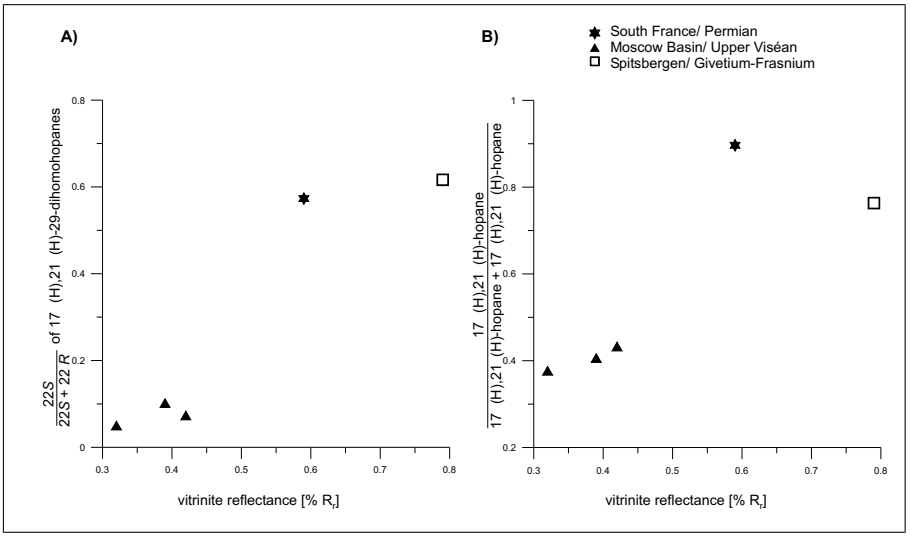

Figure 7.11: Cross plots of A) $22S/22S + R$ of 17α(H),21β(H)-29-dihomohopane and B) C_{32}-(17α(H),21β(H)-/17α(H),21β(H)- + 17β(H),21α(H))-hopane for type I kerogen samples

Spitsbergen but also the samples from South France have reached equilibrium. This agrees to their relative enhanced maturities. Although the coals from the Moscow Basin are characterised by low maturities, their CPI_{HC} is low (Table 6.1). This results from the depositional conditions strongly influencing this maturity parameter.

Maturity parameters based on aromatic hydrocarbons normally do not depend on the maturity of these type I samples. Most of the commonly applied ratios, in comparison to type II-III samples are characterised by elevated values especially for the samples from the Moscow Basin. Additionally, in contrast to all previously discussed sample sets, maturity parameters show no strong correlation to each other. Therefore they are not regarded here.

Considering the HI *vs.* T_{max} plot, the three coals from the Moscow Basin and the one from Spitsbergen contain type I organic matter (Fig. 7.10 B). The samples are characterised by enhanced proportions of aliphatic hydrocarbons in comparison to aromatic hydrocarbons. The kerogen typing for samples from South France is limited due to the lack of Rock-Eval pyrolysis data. Nevertheless both the geology of the three samples and the composition of extractable organic matter for two of them shows relatively high amounts of aliphatic hydrocarbons (Fig

6.1). This supports a type I composition of kerogen. The third one equally to the type II-III coal from the Moscow Basin seems to be characterised by a strong biodegradation, probably accounting for elevated proportions of aromatic hydrocarbons (Fig. 6.1). However this sample is of little value due to the absence of all compounds investigated in this study except *n*-alkanes, -fatty acids, pristane and phytane.

Ratios of pristane/phytane except for the Devonian coal do not correlate to terrestrial derived organic matter deposited under oxic conditions but more strongly indicate a lacustrine or marine origin. This at least for four samples is supported by the ratio of pristane/$n-C_{17}$ indicating a strong marine input of organic matter. According to ratios of alkyldibenzothiophenes to -phenanthrenes and -dibenzofurans none of the samples can be attributed to an unambiguous marine origin. While alkyldibenzothiophenes have not been quantified in the samples from South France, they were generally minor contributors to the rest of the samples which in case of the Moscow coals corresponds to a lacustrine sulphate-poor depositional environment, while for the Spitsbergian coal a fluvio deltaic depositional environment can be suggested (Fig. 6.24, 6.29).

Aliphatic Hydrocarbons in Type I Kerogen Samples

It has been mentioned above, that due to their kerogen composition at least the samples from the Moscow Basin contain enhanced proportions of aliphatic hydrocarbons. They, in contrast to all other samples are characterised by relative enriched proportions of hopanes in comparison to *n*-alkanes. Additionally hopane isomers show wider variations for these samples. Actually they are, besides the less mature type III coal from the Moscow Basin, the only ones characterised by the presence of 2-methylhopane, $\beta\beta$-hopanes and a complete series of hop-17(21)-enes and a higher variability in isomers of tetracyclic secohopanes. Especially the relative amounts of C_{25}-tetracyclic triterpanes to C_{24}-tetracyclic triterpanes, despite the kerogen typing are significantly enhanced for the immature samples (Fig. 7.12). While individual hopenes and hopanes are relatively enriched for the type I coals from the Moscow Basin, the fraction of aliphatic hydrocarbons of

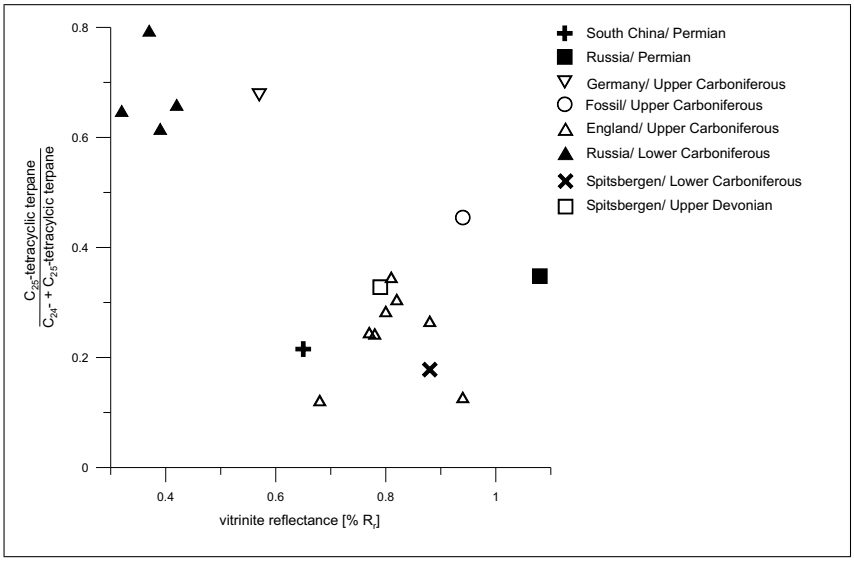

Figure 7.12: Dependence of the distribution of C_{24}- and C_{25}-tetracyclic triterpanes on the maturity of the sediments

the III coal from the Moscow Basin is dominated by long-chain *n*-alkanes. This significant contribution from waxy compounds strongly distinguishes the type III coal from the type I analogues. The three type I coals despite their low maturity show no strong CPI_{HC} and CPI_{FA}. While for the CPI_{HC} this can be attributed to an enhanced contribution of reduced *n*-fatty acids, this does not account for the CPI_{FA}. Although reduction due to depositional environment probably influences the relative amounts, the original pattern is supposed to consist. Therefore it can be suggested, that *n*-fatty acids from both marine and terrestrial sources are minor contributors to the type I coals originating from the Moscow Basin.

7.2 Alkylnaphthalenes and -Phenanthrenes: Biogenic Significance and Relationship of Aromatic Hydrocarbons and Functionalised Analogues

7.2.1 Group I

In the North English coals, compounds based on the naphthalene skeleton were present in the aromatic hydrocarbon fraction, the low-polarity NSO compound fraction and the acid fraction, while compounds based on the phenanthrene skeleton were detected in the aromatic hydrocarbon fraction and the acid fraction, only (Table 7.1).

The aromatic hydrocarbon fraction of all North English coals is dominated by alkylnaphthalenes and -phenanthrenes. For the majority of the samples summed alkylphenanthrenes are present in higher amounts than summed alkylnaphthalenes. A relative increase in the proportions of alkylphenanthrenes, in contrast to observations of for example Hayatsu *et al.* (1978b) does not correspond to increasing maturity. The six coals which are characterised by enhanced proportions of alkylnaphthalenes show a narrow maturity range (0.8-0.9% R_r). However, it is more likely that the composition of the aromatic hydrocarbon fraction represents contribution from a specific source, similar depositional environments or even similar fate during sample preparation.

The low-polarity NSO compound fraction of North English coals is characterised by the presence of alkylnaphthaldehydes and naphthylketones (Table 7.1), while alkylphenanthraldehydes and -phenanthrylketones are absent (or present in not detectable proportions). Corresponding carboxylic acids of both alkylphenanthrenes and -naphthalenes are present in the acid fraction for the majority of these coals (Table 7.1). However, the naphthalenecarboxylic acids are generally present in much higher amounts than the corresponding acids based on the phenanthrene skeleton. Considering, that alkylnaphthalenedicarboxylic acids are also present

Table 7.1: Occurrence of alkylnaphthalenes (N), -phenanthrenes (P), alkylnaphthaldehydes and -naphthylketones (NA/NK), alkylnaphthalenecarboxylic acids (NA), -naphthalenedicarboxylic acids (NDA) and -phenanthrenecarboxylic acids (PA) in the North English coals

Sample	N	P	NA/NK	NA	NDA	PA
E 48388	+++	++	++	++	+	+
E 48389	+++	++	++	++	+	+
E 48390	+++	++	++	++	+	+
E 48214	+++	++	++	++	+	+
E 48216	+++	++	++	++	+	+
E 48220	++	++	++	++	+	+
E 48403	++	++	++	++	+	+
E 48405	++	++	++	n.d.	+	+
E 48392	++	++	n.d.	++	+	+
E 48393	++	++	++	++	+	+
E 48394	++	++	++	n.d.	-	-
E 48395	++	++	++	++	+	+
E 48396	++	++	n.d.	++	+	+
E 48397	++	++	n.d.	n.d.	-	-
E 48398	++	++	++	++	+	+
E 48400	++	++	++	-	+	-
E 48401	++	++	++	-	-	-
E 48382	++	++	++	+	+	+
E 48383	+++	++	++	+	+	+
E 48384	++	++	++	+	+	+

+++:abundant,++:present, +:present to low amounts
-:absent, n.d.:not determined

in the acid fraction of most of the samples, this dominance becomes even more pronounced.

The presence of aromatic hydrocarbons based on the naphthalene and phenanthrene skeleton and their oxygenated analogues arises the question if there is a genetic relationship between these compounds. Assuming that there is a genetic relationship the question is, if the compounds based on the same skeleton were formed at the same time or if one compound class is the precursor while the other is formed by either biotic/abiotic oxidation or reduction. Additionally this relationship at least for the alkylnaphthalenedicarboxylic acids may be even more difficult to assign. Alkylnaphthalenedicarboxylic acids may be precursors

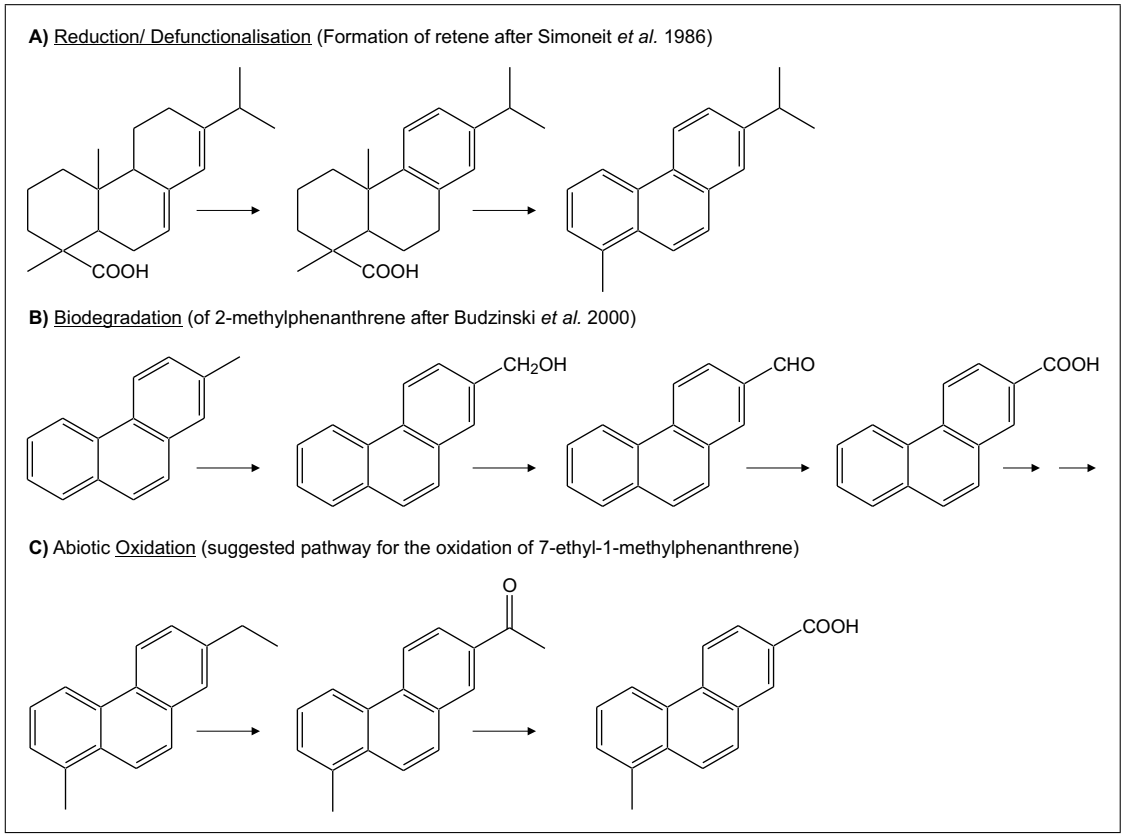

Figure 7.13: Possible genetic relationships between aromatic hydrocarbons and the corresponding ketones, aldehydes and carboxylic acids

of alkylnaphthalenes, their oxidation products or they may originate from the biodegradation of alkylphenanthrenes (Richnow *et al.*, 2000).

It is common agreement, that the formation of aliphatic and aromatic hydrocarbons results from the loss of functional groups in biogenic compounds with increasing maturity (Fig. 7.13 A). Recent studies (Meredith *et al.*, 2000) on the other hand point out, that biodegradation yields in the formation of acid compounds (Fig. 7.13 B). Another likely genetic relationship might be the abiotic oxidation of aliphatic and aromatic hydrocarbons under oxidising conditions. This means a formation of functionalised compounds during deposition or thereafter for example due to increasing maturity (Fig 7.13 C). All three pathways result in the formation of certain compounds accompanied by the loss of others.

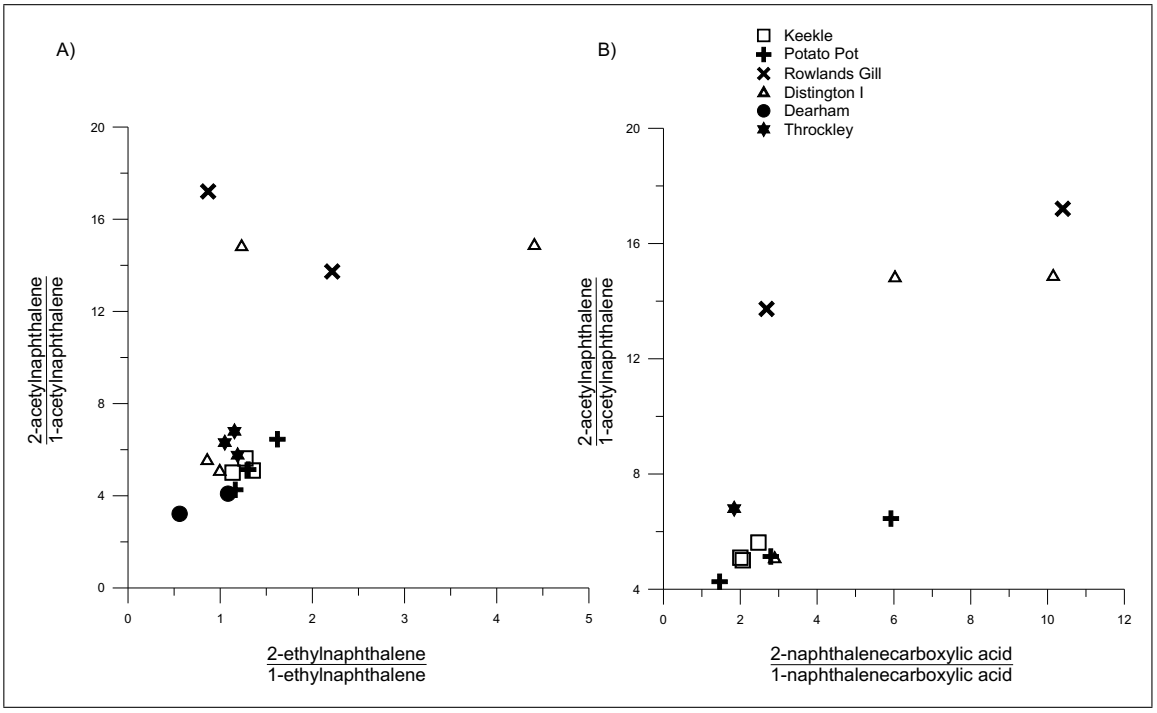

Figure 7.14: Cross plots of the ratios A) 2-ethylnaphthalene/1-ethylnaphthalene *vs.* 2-acetylnaphthalene/1-acetylnaphthalene and B) 2-naphthalenecarboxylic acid/1-naphthalenecarboxylic acid *vs.* 2-acetylnaphthalene/1-acetylnaphthalene

The formation of alkylnaphthalenes and -phenanthrenes from their functionalised analogues is known to be the result of increasing temperature and pressure (Fig. 7.13 A, Formation of retene). The loss of functional groups is attributed to the early stages of coalification. Due to all English coals having passed this stage it is most unlikely that aldehydes, ketones and carboxylic acids should have survived to high amounts. Additionally aromatisation does not unambiguously occur prior to defunctionalisation. The composition of the extractable organic matter of the North English coals however would indicate that aromatisation has proceeded completely while defunctionalisation is a still ongoing process. Another indication that the presence of alkylnaphthalenes and -phenanthrenes does not only result from the ongoing defunctionalisation of functionalised analogues is their composition. While aromatic hydrocarbons with up to four methyl groups are present in high amounts, the functionalised analogues revealed the presence of $C_{(0-1)}$-isomers, only.

The formation of ketones, aldehydes and carboxylic acids based on both the naphthalene and phenanthrene skeleton via biodegradation (Fig. 7.13 B) can probably be excluded. Although carboxylic acids and aldehydes are known to be produced during biodegradation (Zhang and Young, 1997; Wantson *et al.*, 1999; Budzinski *et al.*, 2000), they are supposed to be intermediates, resulting in the formation of low molecular aromatic compounds like salicylic acid, 4- and 5-methylsalycilic acid but also 1,2-naphthalenedicarboxylic acid (Budzinski *et al.*, 2000; Richnow *et al.*, 2000). Additionally the composition of *n*-alkanes, *n*-fatty acids for all North English coals does not indicate enhanced biodegradation. Although *n*-alkanes are characterised by low CPI they predominate the aliphatic fractions. For *n*-fatty acids the biogenic distribution is still recognisable, indicating that these compounds have not been subject to significant biodegradation. Within the distribution of dimethylnaphthalenes, 1,6-dimethylnaphthalene, the one showing the highest susceptibility to biodegradation (Bastow *et al.*, 1999) often is predominant. 2-Ethylnaphthalene is generally present in higher amounts than 1-ethylnaphthalene. The former compound is believed to be biodegraded preferentially (Ahmed *et al.*, 1999). These observations indeed support the hypothesis that the formation of alkylnaphthalene- and -phenanthrene carboxylic acids but also the corresponding aldehydes and ketones via biodegradation is most unlikely.

The formation of aldehydes, ketones and carboxylic acids via abiotic oxidation of the corresponding aromatic hydrocarbons during deposition or thereafter in contrast is supported by different evidences. The oxidation of organic compounds requires the presence of oxidants. At the early stages of diagenesis free oxygen might be still available while it is questionable if aromatisation has proceeded strongly. Although free oxygen might not be available at later stages of deposition other oxidants may be frequently present. The fact that the majority of the North English coals, according to their ratio of pristane/phytane are supposed to have been deposited under oxic conditions, indeed reveals the possibility that oxidising reagents have been available. The possibility of reaction mechanisms like base catalysed auto oxidation has already been suggested by Bennett and Larter (2000) in connexion with the formation of alkylfluoren-9-ones. By analogy the benzylic carbon atom in ethylnaphthalenes, is also highly activated for oxidation. Although correlation of the ratios 2-ethylnaphthalene/1-ethylnaphthalene and 2-

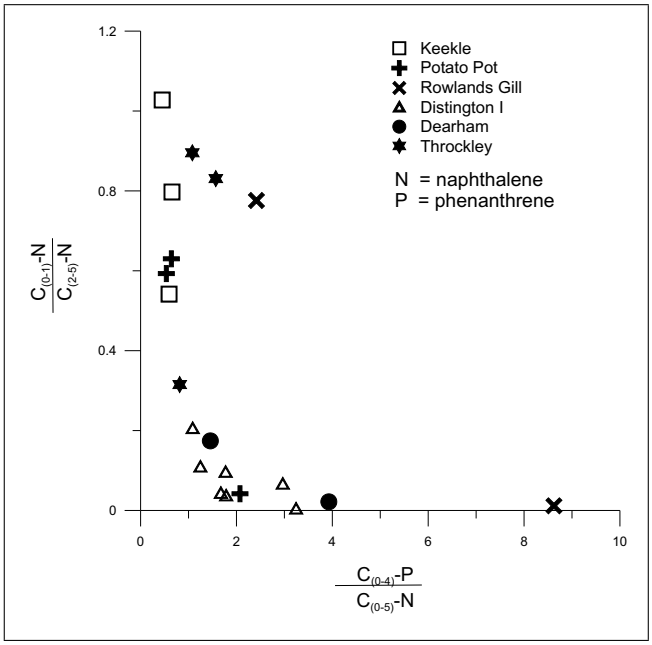

Figure 7.15: Cross plot showing the effect of volatilisation on the relative amounts of alkylphenanthrenes to -naphthalenes

acetylnaphthalene/1-acetylnaphthalene (Fig. 7.14 A) for North English samples is not as strong as the one for the complete sample set (Fig. 6.38) it still reveals, that a good relationship between the two ratios exists. Additionally ethylnaphthalenes generally do not correlate to any other compound for North English samples except the corresponding naphthylketones. A formation of naphthylketones via oxidation of ethylnaphthalenes therefore is proposed here.

In general the ratio of 2-/1-acetylnaphthalene and 2-/1-ethylnaphthalene (Fig. 7.14A) differ in magnitude indicating that 2-ethylnaphthalene might be more susceptible to oxidation than 1-ethylnaphthalene. Sterical hinderance according the oxidation of 1-ethylnaphthalene may result in an enhanced formation of 2-acetylnaphthalene in comparison to 1-acetylnaphthalene. Four samples are characterised by an even stronger predominance of 2-acetylnaphthalene. These samples show low pristane/phytane ratios but highest amounts of sulphur (Table A.1). Although the pristane/phytane ratios indicate that the depositional environment at the beginning of deposition has not been strongly oxidising, it is possible that the availability of sulphur for example in the form of sulphate may be a strong oxidation agent. This would necessarily mean, that not all of the sulphur has been

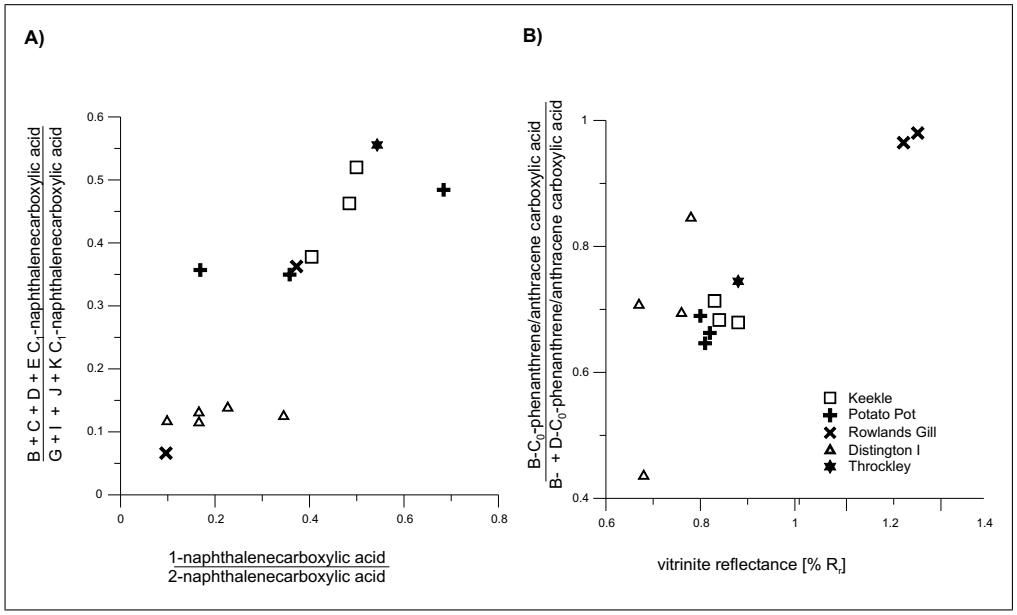

Figure 7.16: Cross plots displaying A) the correlation of (1-/2-)-naphthalenecarboxylic acid to corresponding C_1-naphthalenecarboxylic acids and B) the correlation of B- and D-phenanthrene/anthracenecarboxylic acids to vitrinite reflectance

reduced at the stage where pristane and phytane are formed. Additionally, two of the samples are characterised by enhanced maturities which therefore might also reveal an influence.

The formation of alkylnaphthalenecarboxylic acids in turn may result from further oxidation of naphthylketones or naphthaldehydes due to thermal stress. This oxidation could proceed via a kind of Baeyer-Villiger-oxidation. Reactions of the Baeyer-Villiger type are known to occur in nature and represent oxidations involving peroxycarboxylic acid. Normally the shift of the substituent showing the higher ability to stabilize the carbenium-ion-intermediate is observed (Fig. 7.17). However due to sterical hinderance the migration of the other group may also be favoured. Based on the classical Baeyer-Villiger mechanism only the oxidation of alkylnaphthaldehydes is supposed to result in the corresponding alkylnaphthalenecarboxylic acids (Fig. 7.17). However the correlation for alkylnaphthalenecarboxylic acids and naphthylketones is stronger than for alkylnaphthalenecarboxylic acid and alkylnaphthaldehydes indicating that indeed sterical factors may strongly influence the reaction. It is assumed that the formation of alkylnaphthalenecarboxylic acids results from the abiotic oxidation of both

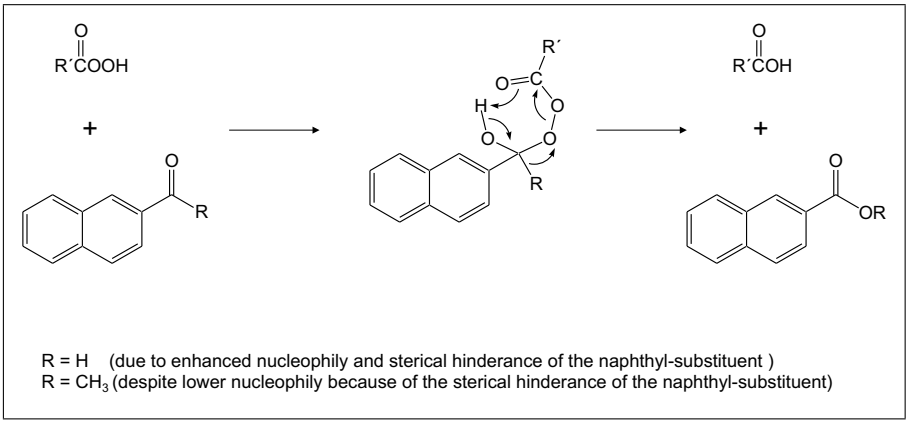

Figure 7.17: Scheme showing the mechanism of the Baeyer-Villiger-oxidation; due to the nucleophily normally hydrogen of the naphthylaldehyde or the naphthyl-substituent of naphthylketones are supposed to shift, while sterical hinderance may explain a preferential shift of the methyl-group

naphthylketones and alkylnaphthaldeyhdes via a kind of Baeyer-Villiger reaction mechanism.

It is most likely that alkylphenanthrenes follow the same oxidation pathway. Therefore the question arises why alkylphenanthraldeyhdes and -phenanthrylketones were at least negligible constituents of the low-polarity NSO compound fraction and why alkylphenanthrenecarboxylic acids in comparison to alkylnaphthalenecarboxylic acids are significantly depleted in the acid fraction. While it is improbable that the different ring numbers of the aromatic hydrocarbons may strongly influence the affinity to oxidation the relative depletion of the functionalised compounds revealing a phenanthrene skeleton has to result from another fact. The most likely explanation is that the relative amounts of alkylnaphthalenes in relation to alkylphenanthrenes may be inexact due to loss of especially $C_{(0-1)}$-naphthalenes via volatilisation. Indeed samples, characterised by high proportions of alkylnaphthalenes also show enhanced proportions of naphthalene and methylnaphthalenes (Fig. 7.15). The lower homologues of alkylnaphthalenes are characterised by relatively low boiling points and therefore may be subject to elevated volatilisation. Actually even the boiling points of dimethylnaphthalenes are significantly lower than the one of phenanthrene and a relative depletion of these compounds can not be ruled out. The observation that lower homologues of alkylnaphthalenes may be subject to volatilisation indicates, that the relative

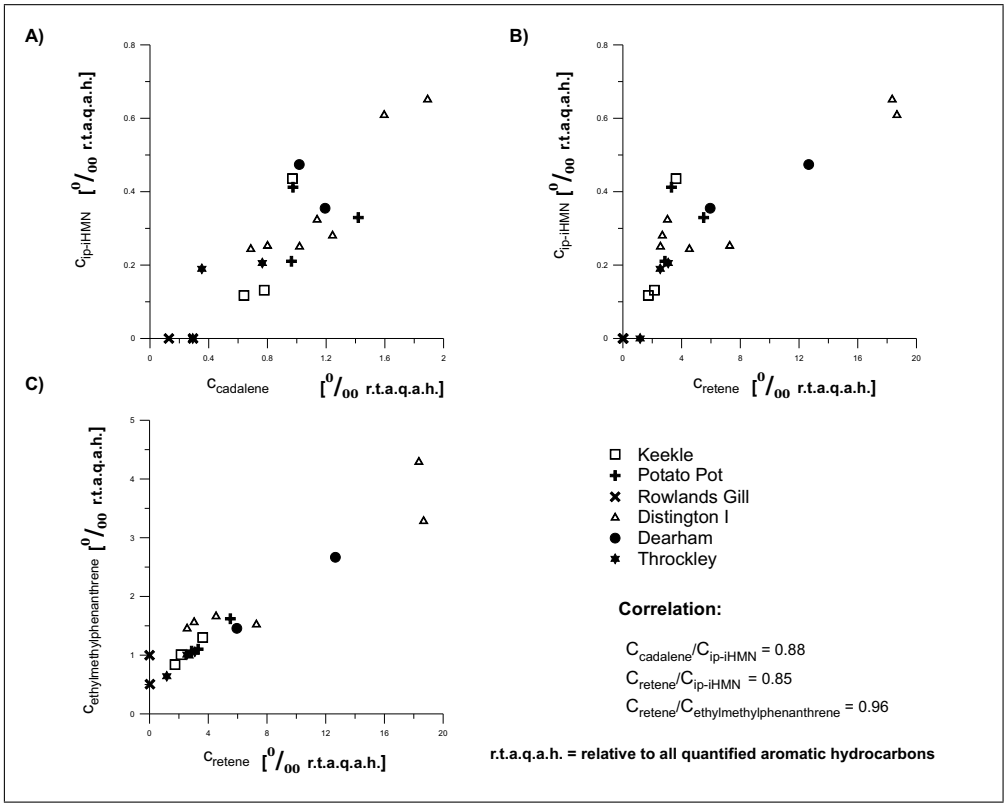

Figure 7.18: Cross plots displaying the correlation for relative amounts of A) cadalene to ip-iHMN, B) retene to ip-iHMN and C) retene to the first eluting ethylmethylphenanthrene

amounts of alkylnaphthalenecarboxylic acids in relation to the analogues based on the phenanthrene skeleton represents the relative contribution of the different compound classes to the extractable organic matter more precise. Nevertheless it should be recognised, that in analogy to the behaviour of aromatic hydrocarbons the amounts of alkylphenanthrenecarboxylic acids to the corresponding acids based on the naphthalene skeleton show no relative increase with increasing maturity of the coals.

While oxidation affected both alkylnaphthalenes and -phenanthrenes, the relative amounts of stable and instable isomers for both classes differs significantly. It is proposed here, that the distribution of alkylphenanthrenes represents the influence of individual biogenic compounds more significantly than the distribution of alkylnaphthalenes. This may seem contradictory to the fact, that maturity parameters of alkylphenanthrenes showed a stronger correlation to vitrinite reflectance

than the one of alkylnaphthalenes. However, although maturity parameters based on alkylphenanthrenes revealed good correlation to the vitrinite reflectance of the North English coals, negative correlations of stable to instable isomers are weak. This indeed indicates that the composition of alkylphenanthrenes is not influenced by isomerisation reactions to the same magnitude than the one of alkylnaphthalenes. For alkylnaphthalenes it should be recognised that there is no unambiguous evidence that they indeed are characterised by lower amounts of biogenic precursors with respect to their original composition. It is most presumable that isomerisation of this compound class occurs prior to the one of alkylphenanthrenes due to an earlier formation. This is well-founded by the fact that aromatisation due to thermal stress proceeds easier for a bicyclic compound than a tricyclic compound. Although it is presumed that at the maturity level of the North English coals the composition of alkylnaphthalenes is less affected by biogenic compounds than the one of alkylphenanthrenes, some alkylnaphthalenes show a behaviour indicating a strong biogenic contribution.

Although alkylnaphthalenes have been subject to volatilisation at least for the majority of the North English coals, relative amounts of isomers probably have retained their original proportions. This is supported by the little variations of boiling points for example of methylnaphthalenes (1-MN: 244°C, 2-MN: 241°C) or dimethylnaphthalenes (bp: 262-270°C). Due to the fact that maturity parameters normally compare the stability of different isomers, volatilisation can not hold for the strong deviations for many of the maturity parameters based on alkylnaphthalenes. Therefore the strong differences in the correlation of alkylnaphthalenes and -phenanthrenes must have another reason.

A strong difference between the two compound classes indeed is that none of the alkylnaphthalenes increases, while some alkylphenanthrenes show an increase with increasing maturity. Except for 1,2,5-, 1,3,6- and 1,3,7-trimethylnaphthalene and the coeluting 1,2,5,6- and 1,2,3,5- tetramethylnaphthalenes all tri- and tetramethylnaphthalenes show a decrease with increasing maturity. In contrast the decrease for higher homologues of alkylphenanthrenes with increasing maturity is less pronounced. It is assumed that destruction of tri- and tetramethylnaphthalenes as the main process at elevated maturities suppresses the effect of ther-

modynamically controlled enrichment of specific isomers. While low homologues of alkylnaphthalenes show no relative increase with increasing rank, both 2- and 3-methylphenanthrene and 2,7- and 2,6-dimethylphenanthrene show a strong increase with increasing maturity. It is possible that the behaviour of low homologues of alkylnaphthalenes is due to different magnitudes in volatilisation of these homologues for individual samples. However, neither an isomer of the corresponding naphthylketones and alkylnaphthaldehydes nor of the naphthalenecarboxylic acids show a relative increase with increasing maturity. In contrast naphthalenecarboxylic acids show a strong correlation between the amounts of 2-naphthalenecarboxylic acid and the corresponding C_1-2-naphthalenecarboxylic acids and the analogues based on the 1-naphthalene skeleton (Fig. 7.16 A). On the other hand two phenanthrene/anthracenecarboxylic acids at least are characterised by a strong correlation to maturity (Fig. 7.16 B). These observations are in good agreement with those on the behaviour of alkylnaphthalenes and -phenanthrenes.

Another important difference between the two compound classes is the correlation of individual isomers. While $C_{(0-2)}$-naphthalenes are characterised by relatively good correlation amongst each other, tri- and tetramethylnaphthalenes with few exceptions show excellent correlation. These correlations are significantly less pronounced for alkylphenanthrenes.

The fact that especially 1,2,5-, 1,3,6- and 1,3,7-trimethylnaphthalene, show weakest correlation to other trimethylnaphthalenes indicates that two different reasons may result in these low correlations being more pronounced for alkylphenanthrenes. First the strong correlations of 1,2,5-trimethylnaphthalene to 1,2,5,6- and 1,2,3,5-tetramethylnaphthalene show, that the amounts of 1,2,5-trimethylnaphthalene are strongly influenced by the magnitude of contribution from a specific biological source. Therefore the weak dependence of amounts of this compound on maturity and other trimethylnaphthalenes can be attributed to the fact, that the proportions are strongly influenced by a specific contribution. The depleted correlation of 1,3,6- and 1,3,7-trimethylnaphthalenes in contrast results from the fact, that these two isomers are the thermodynamically most stable trimethylnaphthalenes and are therefore formed in favour.

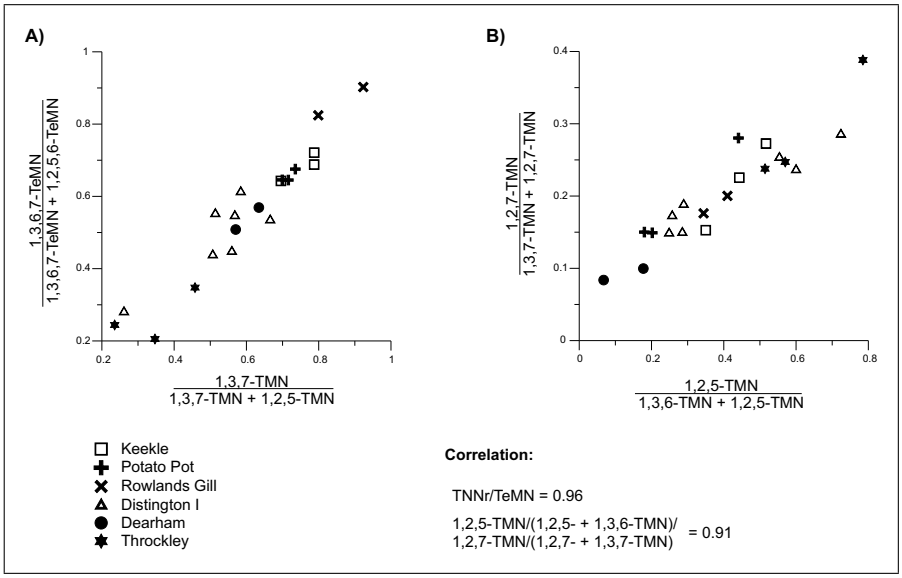

Figure 7.19: Cross plots displaying the correlation of A)TNNr *vs.* TeMN and B) 1,2,5-/1,2,5- + 1,3,6-TMN *vs.* 1,2,7-/1,2,7- + 1,3,7-TMN

In analogy this for the distribution of alkylphenanthrenes would mean either strong differences in thermodynamic stability for different isomers or strong contribution of individual isomers from specific biological sources. The relative thermal stabilities of tetramethylnaphthalenes and dimethylphenanthrenes show similar characteristics (van Duin *et al.*, 1997). Although dimethylphenanthrenes amongst alkylphenanthrenes are characterised by an enhanced correlation of isomers it is still less pronounced than for tetramethylnaphthalenes. While the two thermodynamic most stable isomers 2,6- and 2,7-dimethylphenanthrene indeed show a relative increase at elevated maturities, this does not account for the thermodynamic most stable isomers 1,3,6,7- and 1,3,5,7-tetramethylnaphthalene. Additionally the two tetramethylnaphthalenes show a good correlation to other isomers. The latter observation may account for the fact that isomerisation of alkylnaphthalenes occurs prior to the one of alkylphenanthrenes. However the fact that C_2-phenanthrenes show neither strong positive nor strong negative correlation additionally points to a contribution of specific isomers from biogenic sources, still recognisable at the maturity range of the North English coals.

Although the low correlations of isomers do not generally point to biogenic precursors, some biogenic significance especially for correlating compounds

can be assumed. Retene for example does not strongly depend on 1,7-dimethylphenanthrene but on the first eluting C_3-phenanthrene, which based on its mass spectra is supposed to be an ethylmethylphenanthrene. It is most likely that destruction of retene results in the formation of 7-ethyl-1-methylphenanthrene (Fig. 7.18 C), which by retention index (pers. com. H. Willsch, FZ-Jülich) probably elutes early. The good correlation between the two compounds however (Fig. 7.18 C) indicates, that their thermodynamic stability does not differ strongly and that retene is transformed into 7-ethyl-1-methylphenanthrene immediately. They then probably are preferentially converted into more stable isomers like 1,7-dimethylphenanthrene. Although no strong negative correlation between 1,7-dimethylphenanthrene and the other two compounds is found, this does not generally neglect a relationship but may result from the fact, that 1,7-dimethylphenanthrene has an additional biogenic source.

Additionally a loss of biogenic information within the maturity range of the North English coals however has already occurred. The strong correlation of retene, cadalene and ip-iHMN (Fig. 7.18 A and B) for example is supposed to correspond to the depleted thermodynamic stability of these compounds. They are least abundant for the most mature samples from Rowlands Gill (Fig. 7.18). However strong differences in relative amounts especially for the two samples from Dearham indicate, that within the investigated maturity range, enhanced contribution is still recognisable.

In analogy this, to some extend does also account for correlations between biogenic compounds and non-biogenic compounds of similar thermodynamic stability. Although 1,2,5-trimethylnaphthalene does not strongly correlate to isomers of similar thermodynamic stability, isomerisation reactions in the mobile phase do affect these isomers to same extents (Fig. 7.19 B). This actually does explain the good correlation between 1,2,7-trimethylnaphthalene/1,2,7- and 1,3,7-trimethylnaphthalene *vs.* 1,2,5-trimethylnaphthalene/1,2,5- and 1,3,6-trimethylnaphthalene. The plot therefore at least for the North English coals does not indicate a biogenic relationship between 1,2,7- and 1,2,5-trimethylnaphthalene.

To assess the importance of isomerisation reactions due to both thermal maturity and mobile phase the behaviour of the samples from Throckley is significant (Fig.

7.19). The deviations for these samples are obvious for the majority of the maturity parameters based on aromatic hydrocarbons. This may be explained by the hypothesis that the composition of the organic matter in samples from Throckley is characterised by an immaturity not represented by vitrinite reflectances and T_{max}. It is suggested that the mobile phase of these samples in comparison to the rest of the North English coals is weak and that the most likely explanation is a fast heating up period in this specific location.

7.2.2 Group II

In analogy to the North English coals, alkylnaphthalenes and -phenanthrenes for the six immature type II-III coals were generally abundant (Table 7.2) but show strong differences in distribution. This results from the fact that aromatic hydrocarbons often are formed and subject to isomerisation at elevated temperatures, only. Correlation of different alkylnaphthalenes and -phenanthrenes for low maturity samples indicates biogenic relationships more strongly.

In correspondence to the North English coals the relative amounts of alkylphenanthrenes to alkylnaphthalenes are mainly influenced by volatilisation effects of $C_{(0-1)}$-naphthalenes (Fig. 7.20 A) and not by maturity effects. Nevertheless the two coals from Germany are characterised by significantly enhanced proportions of alkylnaphthalenes in comparison to alkylphenanthrenes although the two samples show a significant depletion of $C_{(0-1)}$-naphthalenes (Fig. 7.20 A).

Alkylnaphthaldehydes and alkylnaphthylketones were present in all of the six samples (Table 7.2). However, 1-acetylnaphthalene has not been quantified in the Spitsbergian coal due to low proportions of the generally weak low-polarity NSO compound fraction for this sample. The analogue compounds based on the phenanthrene skeleton, again were generally not detected.

Table 7.2: Occurrence of alkylnaphthalenes (N), -phenanthrenes (P), alkylnaphthaldehydes and -naphthylketones (NA/NK), alkylnaphthalenecarboxylic acids (NA), -naphthalenedicarboxylic acids (NDA) and -phenanthrenecarboxylic acids (PA) in immature type III organic matter

Sample	N	P	NA/NK	NA	NDA	PA
E 49710	++	++	++	-	-	-
E 48996	++	++	++	-	-	-
E 48988	++	++	++	++	+	-
E 48989	++	++	++	-	+	-
E 48993	++	++	++	-	-	-
E 48991	++	++	++	-	-	-

++:present, +:present to low amounts, -:absent

This does also account for alkylphenanthrenecarboxylic acids (Table 7.2). Alkylnaphthalenecarboxylic acids in contrast were present in the biodegraded coal from the Moscow Basin, while four C_{0-1}-alkylnaphthalenedicarboxylic acids were

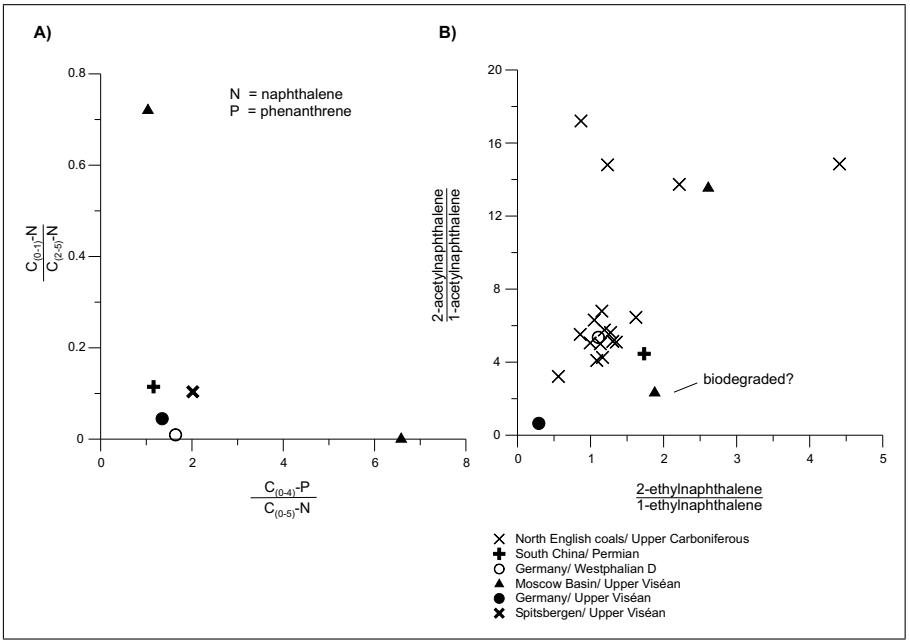

Figure 7.20: Cross plots showing A) the effect of volatilisation on the relative amounts of alkylphenanthrenes to -naphthalenes and B) the ratio of 2-ethylnaphthalene/1-ethylnaphthalene *vs.* 2-acetylnaphthalene/1-acetylnaphthalene

present in both coals from the Moscow Basin (Table 7.2). Although the relative amounts of 2-acetylnaphthalene and 1-acetylnaphthalene to the ratio of the corresponding ethylnaphthalenes show good correlation for these samples in general, this does least account for the biodegraded sample from the Moscow Basin (Fig. 7.20 B). It is the only one of the whole set in which the relative amounts of acetylnaphthalene and ethylnaphthalene isomers are almost identical.

The findings generally support the hypothesis that oxidation of ethylnaphthalenes to the corresponding acetylnaphthalenes occurs easily and does not require enhanced thermal stress. The relative enhanced proportions of 2-acetylnaphthalene are analogue to the ratios for the North English samples (Fig. 7.20 B). In this context they were proposed to result from a preferential oxidation of 2-ethylnaphthalene. The absence of alkylnaphthalene- and -phenanthrenecarboxylic acids supports the hypothesis that these compounds are formed at elevated temperatures, only. However the presence of carboxylic acids based on the naphthalene skeleton in the acid fraction for coals from the Moscow Basin indicates that oxidation due to thermal stress and the presence of oxidants is not the only pathway

resulting in the formation of these compounds. The fact that especially for the biodegraded sample the ratio of 2-acetylnaphthalene to 1-acetylnaphthalene is almost identical to the relative proportions of the corresponding ethylnaphthalenes indicates a formation pathway different to the one for the other coals. The ratio of the corresponding alkylnaphthalenecarboxylic acids is also of the same magnitude. For this specific sample biodegradation might yield in alkylnaphthaldehydes and naphthylketones, while both 1- and 2-ethylnaphthalene then are supposed to show no strong differences in susceptibility. This is in contrast to the findings of Ahmed *et al.* (1999), who observed a preferential degradation of 2-ethylnaphthalene. Nevertheless the distribution of aliphatic hydrocarbons, for example the CPI_{HC} and the ratio of pristane/$n - C_{17}$ besides the reducing environments may also point to a significant alteration because of biodegradation. The coal, contrary to its low thermal maturity is characterised by significantly enhanced proportions of aromatic hydrocarbons although it has been deposited in reducing environments. In comparison to the second sample from the Moscow Basin, this sample exhibited lower amounts of type III kerogen, this supporting that biodegradation has especially affected aliphatic hydrocarbons. However also for the second sample from the Moscow Basin the presence of alkylnaphthalenedicarboxylic acids is suggested to point to biodegradation.

For the six samples of this group strong biogenic relationships are observed for both the group of alkylnaphthalenes and -phenanthrenes. Indicated by the low correlation of maturity parameters for aromatic hydrocarbons to vitrinite reflectances, except for MPIs, composition of alkylnaphthalenes and -phenanthrenes is not significantly influenced by maturity. Besides an insignificant depletion of compounds like phenanthrene, naphthalene and methylnaphthalenes none shows an unambiguous depletion for the more mature samples of this subset. In contrast some of the tri- and tetramethylnaphthalenes but also of higher phenanthrene homologues show an increase. This is more pronounced for alkylnaphthalenes and at least for the tetramethylnaphthalenes shows no dependence on the relative thermodynamical stability of the isomers (van Duin *et al.*, 1997). These findings are in clear contrast to the depletion of tri- and tetramethylnaphthalenes for the North English samples. This may be explained by the fact that higher homologues are formed at low maturity ranges due to reactions like aromatisation of biogenic precur-

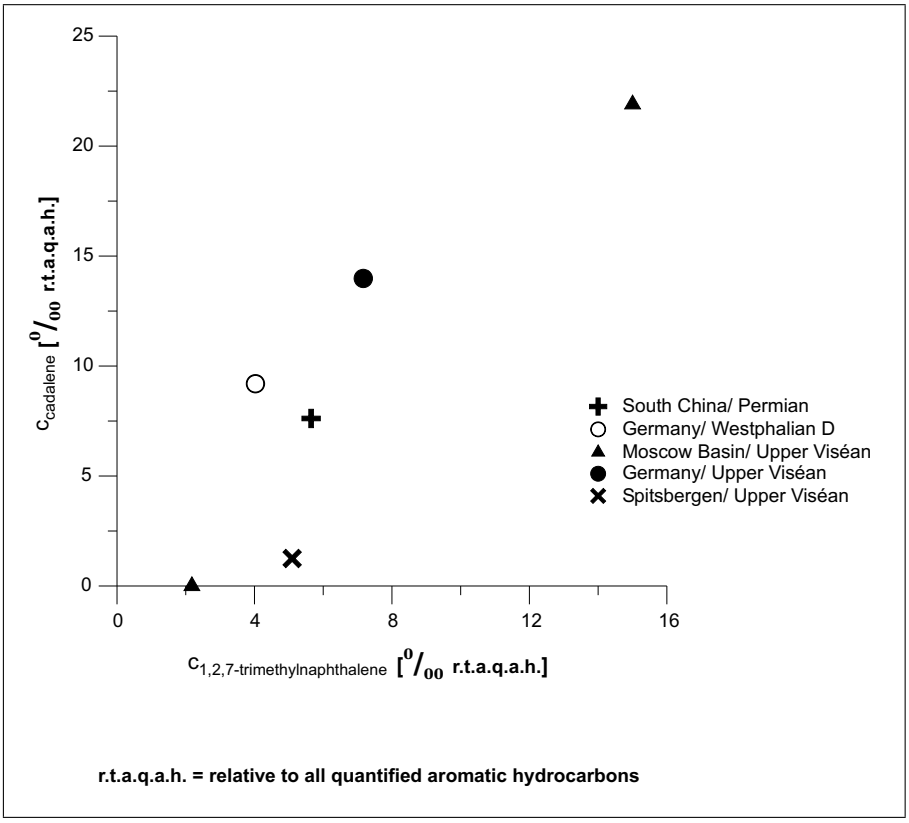

Figure 7.21: Cross plot showing the strong correlation of relative proportions for cadalene and 1,2,7-trimethylnaphthalene also corresponding to the maturity of the samples

sors or methylation. Destruction at higher maturities, then would explain the low variability of tetramethylnaphthalene distribution for the North English. Most significantly, the two coals from Germany are characterised by enhanced proportions of tri- and tetramethylnaphthalenes not resulting from an elevated volatilisation of lower homologues (Fig. 7.20 A). The high proportions of tri- and tetramethylnaphthalenes may result from two factors. Methylation of $C_{(0-2)}$-naphthalenes may be strong at this maturity level. However, although an increase of higher homologues has generally been observed for the six coals it is most unlikely that the enhanced formation should only strongly affect the two German coals. Another factor may be the contribution of especially tri- and tetramethylnaphthalenes from a specific biogenic source. The two samples, according to steranes and ATR_{HC} are characterised by high proportions of terrestrial organic matter. The distribution of alkylnaphthalenes therefore may show the original contribution more significantly than for other samples. Alkylnaphthalenes are supposed to originate

from sesquiterpenes. These C_{15}-compounds contribute to the C_5-naphthalenes. The relative enhanced amounts of $C_{(2-4)}$-naphthalenes therefore may be due to the fact that demethylation of biogenic compounds has not strongly proceeded for the two German coals. This is supported by the fact that the two samples are the only ones of the hole set where anthracene, 1- and 2-methylanthracene were present in same amounts than the corresponding $C_{(0-1)}$-phenanthrenes. The former compounds are present in terrestrial organic matter (Streibl and Herout, 1969). Alkylanthracenes in comparison to alkylphenanthrenes are characterised by a depleted thermal stability. Their presence in the two German samples therefore indeed supports the hypothesis that organic matter has not been subject to intensive thermal alteration.

While biogenic relationships especially for alkylnaphthalenes for the North English coals were difficult to assign this may be possible due to the composition espe-

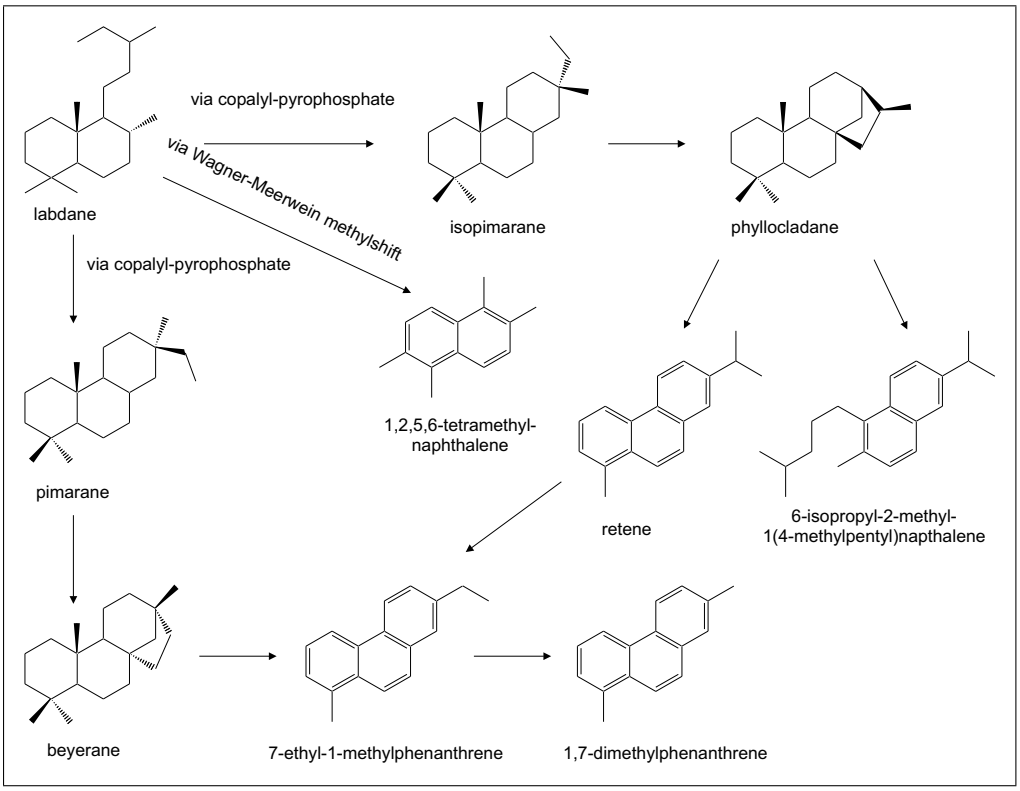

Figure 7.22: Possible biogenic relationship between retene, ip-iHMN, 7-ethyl-1-methylphenanthrene and 1,2,5,6-tetramethylnaphthalene after King and de Mayo (1964); Ellis *et al.* (1996); Otto and Wilde (2001)

cially of the two German coals. Correlations of isomers are still stronger for alkylnaphthalenes than for alkylphenanthrenes. Nevertheless they are significantly less pronounced for trimethylnaphthalenes and therein especially for 1,2,4- and 1,2,7-trimethylnaphthalene. These two isomers, besides 1,2,5-trimethylnaphthalene probably are the least stable ones.

Amongst the biomarkers, cadalene shows a good correlation to 1,2,7-trimethylnaphthalene (Fig. 7.21) but not to ip-iHMN and retene. The latter two compounds again are characterised by a strong correlation. In agreement to the observations for the North English coals, ip-iHMN and retene show no correlation to 1,7-dimethylphenanthrene but to the first eluting ethylmethylphenanthrene, probably 7-ethyl-1-methylphenanthrene. While the dependence of 1,2,5-trimethylnaphthalene on 1,2,5,6-tetramethylnaphthalene in contrast to the North English coals is weak, the latter compound shows strong correlation to retene and ip-iHMN. 1,2,5-Trimethylnaphthalene strongly corresponds to 1,7-dimethylphenanthrene (Fig. 7.23). The correlation of 1,2,7-trimethylnaphthalene and cadalene can neither be explained by the formation of both compounds via cyclisation of farnesol nor from isomerisation reactions of cadalanes and therefore is attributed to a slight dependence of both compounds on maturity. Indeed the amounts of 1,2,7-trimethylnaphthalene and cadalene are weakest for the more mature samples of South China and Spitsbergen. However due to cadalene being a biomarker, a biogenic relationship can not be ruled out.

In contrast the correlation of retene, ip-iHMN, the first eluting ethylmethylphenanthrene and 1,2,5,6-tetramethylnaphthalene may result from a rather complex formation pathway (Fig. 7.22). The formation of retene and ip-iHMN from phyllocladanes at elevated temperatures with palladium on carbon as a catalyst has been performed by Ellis *et al.* (1996). Phyllocladanes but also beyeranes are formed from isopimaranes and pimaranes via cyclisation (Otto and Wilde, 2001). The formation of 7-ethyl-1-methylphenanthrene from compounds of the pimarane or isopimarane type has also been reported by Ellis *et al.* (1996). Additionally it can also derive from degradation of retene, due to the instability of the isopropyl group. The formation of 1,2,5,6-tetramethylnaphthalenes from compounds of the pimarane or isopimarane type on the other hand might proceed via dehydrogena-

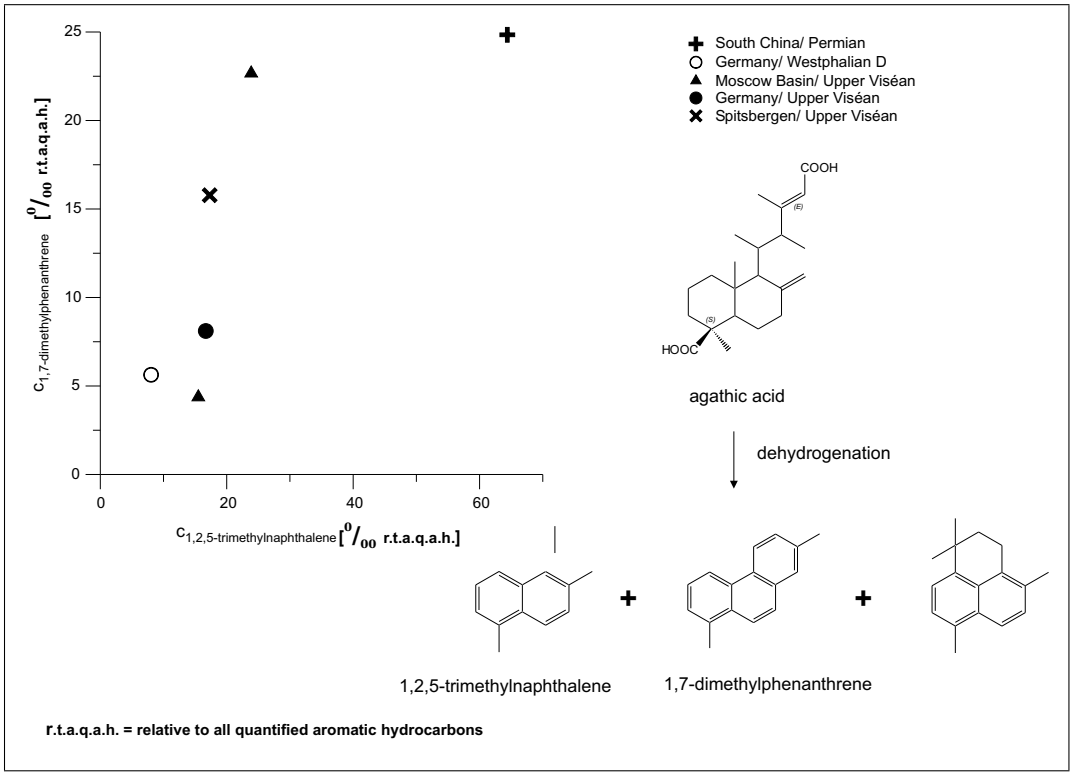

Figure 7.23: Cross plot showing the good correlation of relative proportions for 1,7-dimethylphenanthrene and 1,2,5-trimethylnaphthalene and the most likely formation of both via dehydrogenation of agathic acid after King and de Mayo (1964)

tion of compounds like isopimara-9(11),15-diene-3β,19-diol. The loss of a methyl group is prevented via preliminary Wagner-Meerwein shift (King and de Mayo, 1964). The reaction depends on the availability of an adjacent kationic site, which indeed is present in the isopimarane-diol. The formation of especially retene from phyllocladane is supported by the fact, that retene was present in the coal originating from South China while dehydroabietic acid was absent.

While 1,7-dimethylnaphthalene shows no correlation to retene it strongly corresponds to 1,2,5-trimethylnaphthalene (Fig. 7.23). Good correlation between these two compounds strongly indicates that they are formed via dehydrogenation of agathic acid (King and de Mayo, 1964). A formation of the two compounds via dehydrogenation of manool in contrast would additionally lead to enhanced proportions of 1,6-dimethylnaphthalene. This however is not observed.

7.2.3 Group III

In analogy the previously discussed subsets, alkylnaphthalenes and -phenanthrenes dominate the fraction of aromatic hydrocarbons for the mature type II-III samples (Table 7.3). The predominance of alkylphenanthrenes in comparison to the previously discussed coals is more pronounced for these relatively mature samples. It does not correspond to volatilisation effects (Fig. 7.24 A) and is most significant for the mature fossil (Table 7.3), which therefore is not shown in the plot. These findings indicate, that at elevated thermal maturities, the amounts of alkylphenanthrenes regarding Hayatsu *et al.* (1978b) show a relative increase.

Naphthylketones and alkylnaphthaldehydes were abundant in all seven samples except for the Russian one (Table 7.3). Their absence in this sample probably results from the weakness of its low-polarity NSO compound fraction. While the presence of alkylnaphthaldehydes and naphthylketones in the less mature coals indicated, that they are formed easily, their presence in the more mature samples shows, that they persist elevated thermal stress due to an enhanced thermodynamic stability. The relative amounts of 2-/1-naphthylketone to 2-/1-ethylnaphthalene for the seven samples are in good agreement with those of previously discussed coals (Fig. 7.24 B). They show no dependence on the redox conditions of deposition.

Due to the absence of ethylnaphthalenes for one sample from East Greenland and the *Mesocalamites cf. Taitianus*, the correlation was only established for four of the seven samples. The two samples, according to the vitrinite reflectance are supposed to be the most mature ones of this subset. It is presumable that the absence of ethylnaphthalenes results from the destruction of this compounds via either demethylation/deethylation or oxidation. The sediment from East Greenland is one of those where the relative amounts of $C_{(0-1)}$-naphthalenes have not been depleted significantly (Fig. 7.24 A). Therefore volatilisation of ethylnaphthalenes can not hold for their absence.

Although it has been presumed for the North English coals, that the presence of carboxylic acids based on the phenanthrene and naphthalene skeleton results from oxidation reactions of corresponding aldehydes and ketones due to thermal

Table 7.3: Occurrence of alkylnaphthalenes (N), -phenanthrenes (P), alkylnaphthaldehydes and -naphthylketones (NA/NK), alkylnaphthalenecarboxylic acids (NA), -naphthalenedicarboxylic acids (NDA) and -phenanthrenecarboxylic acids (PA) in mature type II-III organic matter

Sample	N	P	NA/NK	NA	NDA	PA
E 49748	++	++	++	-	-	-
E 49749	++	++	++	-	-	-
E 49750	++	++	++	-	-	-
E 49751	++	++	++	+	+	-
E 48990	++	++	-	-	-	-
E 48430	++	++	++	+	+	+
E 48425	++	+++	++	-	+	+

++:present, +:present to low amounts, -:absent

maturation under oxic conditions, these compounds were generally absent in four of the seven samples (Table 7.3). This for three samples from East Greenland may result from the generally depleted proportions of organic matter, while it corresponds to the absence of alkylnaphthaldehydes and naphthylketones in the Russian coal. For the *Mesocalamites cf. Taitianus* the presence of alkylphenanthrene/-anthracenecarboxylic acids, and absence of alkylnaphthalenecarboxylic acids corresponds to the distribution of alkylphenanthrenes to -naphthalenes. The *Sigillaria* is the only sample of the subset characterised by the presence of alkylnaphthalene, -phenanthrene/-anthracene and -naphthalenedicarboxylic acids (Table 7.3). The findings indicate that although the formation of carboxylic acids based on the naphthalene and phenanthrene skeleton may require elevated thermal stress this at a certain magnitude may again result in the destruction of these compounds.

In agreement with the relative amounts for 2-/1-naphthylketones, the ratio of 2-/1-naphthalenecarboxylic acid, for the two most mature samples are relatively depleted (Fig. 7.24 C), this being more pronounced for the sample from East Greenland. The relatively enhanced proportions of compounds of the 1-naphthalenecarboxylic acid skeleton, therefore contradict the thermodynamic stability of compounds based on the two isomers. 1-Naphthalenecarboxylic acid is supposed to be less stable than 2-naphthalene carboxylic acid.

In accordance with its strong influence on maturity parameters (Fig. 7.8 A) the distribution of individual alkylnaphthalenes and -phenanthrenes for the *Meso-*

calamites cf. Taitianus significantly influences many correlations. Therefore the data of this sample have been excluded from further discussion on alkylnaphthalenes and -phenanthrenes. While at least maturity ratios of alkylnaphthalenes showed a correspondence to vitrinite reflectance this does not account for individual alkylnaphthalenes or -phenanthrenes. Some of the more stable trimethylnaphthalenes, however, are characterised by an increase of amounts in relation to T_{max} (the value for the sample showing mineral matrix effect has not been considered), while most of the 1,2-substituted tetramethylnaphthalenes decrease with increasing T_{max}. In contrast correlation of alkylphenanthrenes to T_{max} normally is weak. In general the weak correlations are in strong analogy to the behaviour of maturity parameters based on aromatic hydrocarbons. These findings indicate that the composition of alkylnaphthalenes and -phenanthrenes for the subset of mature type II-III is rather complex and does not depend on their thermal maturity only.

Nevertheless correlation amongst different isomers of alkylnaphthalenes and -phenanthrenes are still more pronounced for these samples than for the subsets that have been discussed previously. This for the alkylnaphthalenes strongly corresponds to the findings for the North English coals and the fact that isomerisation reactions for this compound class had already proceed at lower thermal maturities. The only isomers characterised by weak correlation are the most stable ones i.e. 1,3,7- and 2,3,6-trimethylnaphthalene but also 1,3,6,7-, 2,3,6,7- and sometimes 1,3,5,7-tetramethylnaphthalene (van Duin *et al.*, 1997). While for the previously discussed subsets a specific contribution of 1,2,5-trimethylnaphthalene to the extractable organic matter was often recognisable this does not account for these more mature samples anymore.

Due to the higher thermal maturity alkylphenanthrenes show a better correlation than for the previously discussed coals. However correlation between $C_{(0-2)}$-phenanthrenes and higher homologues is weak. This may account for the differences in thermodynamic stability due to the magnitude of methylation. It is not presumable that it results from strong contributions of specific isomers to the extractable organic matter as none of the isomers is characterised by a weak correlation to other homologues.

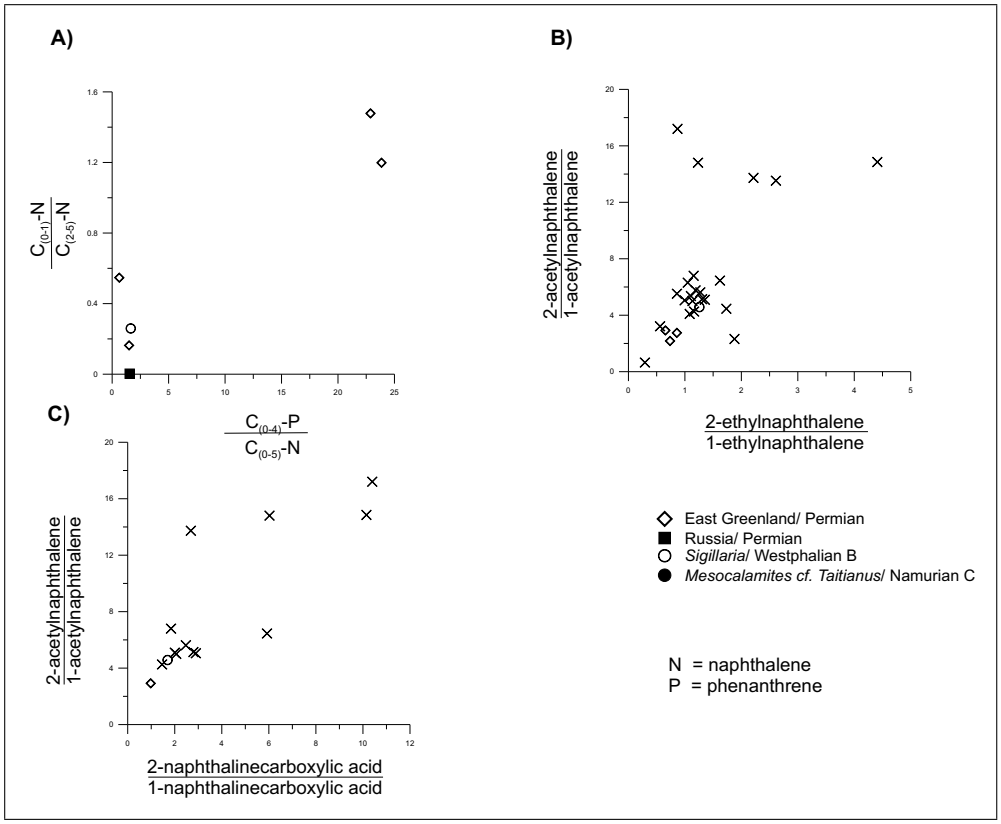

Figure 7.24: A) Influence of volatilisation on the distribution of alkylnaphthalenes and -phenanthrenes, B) the relative amounts of 2-ethylnaphthalene/1-ethylnaphthalene *vs.* 2-acetylnaphthalene/1-acetylnaphthalene and C) the relative amounts of 2-acetylnaphthalene/1-acetylnaphthalene *vs.* 2-naphthalenecarboxylic acid/1-naphthalenecarboxylic acid

According biomarkers, correlation between cadalene, ip-iHMN, retene, 1,2,5-trimethylnaphthalene, pimanthrene and the first eluting ethylmethylphenanthrene are difficult to assign. Retene, pimanthrene but also 1,2,5-trimethylnaphthalene were generally abundant, while ip-iHMN and the ethylmethylphenanthrene could only be quantified in one sample; cadalene in two. In contrast to the North English coals, 1,2,5-trimethylnaphthalene and 1,2,5,6-tetramethylnaphthalene show weak correlation. While ip-iHMN often may be absent due to its low thermal stability, the presence of retene accompanied by the absence of the first eluting ethylmethylnaphthalene is difficult to explain. For the immature coals it has been proposed that the two compounds in comparison to pimanthrene may be characterised by a similar thermodynamic stability. For the subset of mature samples, pimanthrene and retene are characterised by a better correlation than for the previously

discussed samples. This may indicate, that 7-ethyl-1-methylnaphthalene as an instable intermediate is rapidly converted into 1,7-dimethylphenanthrene, while retene is still formed at these elevated maturities. However, correlation of 1,7-dimethylnaphthalene and retene is not too strong, corresponding to either the differences in thermodynamic stability or the magnitude of contribution from different sources, i.e. agathic acid, dehydrabietic acid and phyllocladane. While retene is a transformation product of the two latter precursors, 1,7-dimethylphenanthrene is formed due to destruction of all three natural compounds.

Retene shows a strong positive correlation to T_{max}. For the mature samples T_{max} sometimes showed to be the better maturity parameter. The observations for retene therefore support the hypothesis, that it indeed is released at elevated thermal maturities. Due to its isopropyl group the compound is supposed to show a depleted thermal stability. An enhanced formation of retene from phyllocladane at elevated temperatures, however is improbable. Phyllocladane has not been a major compound of the aliphatic fraction for either of the investigated samples. The formation of retene via cyclisation of ip-iHMN at elevated temperatures in contrast may influence the relative amounts of retene. Nevertheless ip-iHMN may also be transformed into 1,2,6-trimethylnaphthalene or intermediates for example 1,2-dimethyl-6-isopropylnaphthalene.

7.2.4 Group IV

For the immature type I samples alkylphenanthrenes are normally present in higher amounts than the corresponding alkylnaphthalenes. This again results from the volatilisation of especially $C_{(0-1)}$-naphthalenes (Fig. 7.25 A). However, the coal from the Moscow Basin that has not been assigned as cannel-boghead, shows elevated proportions of alkylphenanthrenes in contrast to its relative low magnitude of volatilisation (Fig. 7.25 A). Therefore it can be assumed, that natural precursors showing a phenanthrene skeleton maybe major contributors to the organic matter of this sample.

The presence of alkylnaphthaldehydes and alkylnaphthylketones in the low-polarity NSO compound fraction of all samples, except one from the Moscow Basin and the biodegraded sample from South France (Table 7.4) supports the hypothesis that these compounds are easily formed in sediments. This has been suggested based on the observations made for the previous discussed subsets of samples. Additionally their formation is not restricted to strongly oxic depositional environments. Again in analogy to the previously discussed samples, ratios of naphthylketones strongly correlate to ratios of ethylnaphthalenes (Fig. 7.25 B). The absence of alkylnaphthalene- and -phenanthrenecarboxylic acids for all samples, but the cannel coal from Spitsbergen (Table 7.4), refers to the hypothesis that these compounds are formed at elevated temperatures. Naphthalenedicarboxylic acids are abundant in coals from the Moscow Basin and Spitsbergen (Table 7.4). Although only few isomers were detected this indicates, that they are formed via another pathway than alkylnaphthalene- and -phenanthrenecarboxylic acids. Biodegradation indeed might result in their formation while the fact, that naphthalenedicarboxylic acids have not been found in the biodegraded sample from South France slightly contradicts this hypothesis. Again it can not be ruled out that their absence in this sample has to be attributed to its generally low amounts of extractable organic matter.

In analogy to previously discussed samples, correlations amongst alkylnaphthalenes generally are more pronounced than for alkylphenanthrenes. However in contrast to the immature type II-III coals, the amounts of especially $C_{(0-2)}$-

Table 7.4: Occurrence of alkylnaphthalenes (N), -phenanthrenes (P), alkylnaphthaldehydes and -naphthylketones (NA/NK), alkylnaphthalenecarboxylic acids (NA), -naphthalenedicarboxylic acids (NDA) and -phenanthrenecarboxylic acids (PA) in immature type I organic matter

Sample	N	P	NA/NK	NA	NDA	PA
E 48478	++	++	++	-	-	-
E 48479	++	++	++	-	-	-
E 48480	++	++	-	-	-	-
E 48985	++	++	-	-	+/-	+
E 48986	++	++	++	-	+/-	+
E 48987	++	++	++	-	+/-	+
E 48992	++	++	++	+	+/-	+

++:present, +:present to low amounts, -:absent
+/-:few isomers present

naphthalenes generally increase with increasing maturity, despite the fact that these compounds are affected by volatilisation. Although in analogy to the immature type II-III samples C_3-naphthalenes normally show an increase due to elevated thermal maturities, this does not account for the relatively stable isomers, i.e. 1,3,7-, 1,3,6- and 2,3,6-trimethylnaphthalene. The findings support the hypothesis based on the previous discussed subsets, that isomerisation reactions for alkylnaphthalenes occur prior to the ones for alkylphenanthrenes. However at the maturity level of both the immature type II-III coals and the immature type I samples the formation of C_{3-4}-naphthalenes and therefore their contribution to the mobile phase is the predominant factor affecting their composition.

While the amounts of $C_{(0-2)}$-phenanthrenes normally are characterised by a relative decrease with increasing maturity, this does not account for 9-methylphenanthrene, which increases with increasing maturity. These findings correlate to a marine origin of organic matter (Budzinski *et al.*, 1995). The relative amounts of this compound actually may strongly influence the MPIs accounting for the weak correlation.

For the biomarkers, in correspondence to type II-III samples, cadalene, 1,2,7-, and 1,2,5-trimethylnaphthalene show weak correlation to alkylnaphthalenes. The strong correlation between 1,2,7-trimethylnaphthalene and cadalene, accords to their behaviour for the low maturity type II-III coals. This strongly indicates,

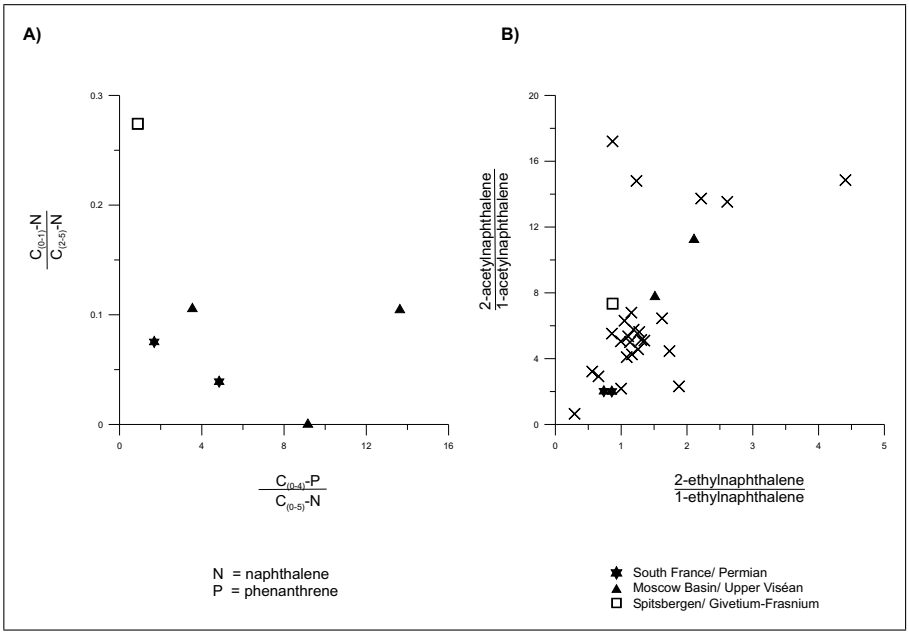

Figure 7.25: A) Influence of volatilisation on the distribution of alkylnaphthalenes and -phenanthrenes and B) relative amounts of 2-ethylnaphthalene/1-ethylnaphthalene *vs.* 2-acetylnaphthalene/1-acetylnaphthalene

that this is not due to their low thermal stability only, but indeed to a biogenic relationship. However the precursors of 1,2,7-trimethylnaphthalene are unknown.

In contrast to the low maturity type II-III coals, 1,7-dimethylphenanthrene and 1,2,5-trimethylnaphthalene show a weak correlation. Agathic acid, the suggested precursor of the two compounds therefore may be a minor contributor to the organic matter of the type I samples.

While ip-iHMN was not generally detected, retene was. It is characterised by a good correlation to 1-methylphenanthrene. However this is of little significance because a correlation to 1,7-dimethylphenanthrene and the suggested 7-ethyl-1-methylphenanthrene is not observed. Although correlations for these compounds are weak, the presence of cadalene and retene indicates, that organic matter from terrestrial sources did also contribute to the organic matter of the type I samples. Additionally it may be suggested that due to the elevated input of marine organic matter the terrestrial biogenic relationships are less recognisable.

7.3 Significance of Alkylfluorenes, -Biphenyls, -Phenylnaphthalenes and -Fluoren-9-ones

7.3.1 Group I

While natural precursors for many alkylnaphthalenes and -phenanthrenes are known, alkylfluorenes, -biphenyls and -phenylnaphthalenes lack direct potential biogenic precursors. The three compound classes often have been supposed to be formed via unspecific radical coupling (Fig. 7.26 A + B) (Alexander *et al.*, 1988; Kagi *et al.*, 1990; Alexander *et al.*, 1994; Marynowski *et al.*, 2001). Although it has been suggested that carbohydrates are precursors of alkylphenylnaphthalenes and phenolic lignin derivatives of alkylbiphenyls (Takatsu and Yamamoto, 1993; Alexander *et al.*, 1994), the geosynthetic processes i.e. radical phenylation result in the loss of the biogenic information (Fig. 7.26 A).

The radical coupling of alkylfluorenes is due to the cyclisation of *ortho*-substituted alkylbiphenyls (Fig. 7.26 B). However, a corresponding depletion of alkylbiphenyls has not been observed (Alexander *et al.*, 1988; Willsch and Radke, 1995). The formation of free radicals normally is induced photochemically or thermally and suppressed by polar liquid phases. An increase of temperatures prior to or during deposition of organic matter therefore is supposed to enhance proportions of radically formed compounds. In correspondence to Alexander *et al.* (1994) and Marynowski *et al.* (2001), oxygen strongly favours the formation of phenyl groups.

The generation of alkylfluoren-9-ones on the other hand, is supposed to proceed via two pathways. Oxidation of alkylfluorenes is induced thermally or photochemically and does not depend on the presence of catalysts. Intramolecular Friedel-Crafts acylation of carboxybiphenyls on the other hand does not require oxic conditions but the presence of catalysts (Fig. 7.26 C).

In contrast to alkylnaphthalenes and -phenanthrenes, alkylfluorenes, -biphenyls and -phenylnaphthalenes are minor contributors to the fraction of aromatic hydrocarbons of all North English coals (Table 7.5). The oxygenated analogues of

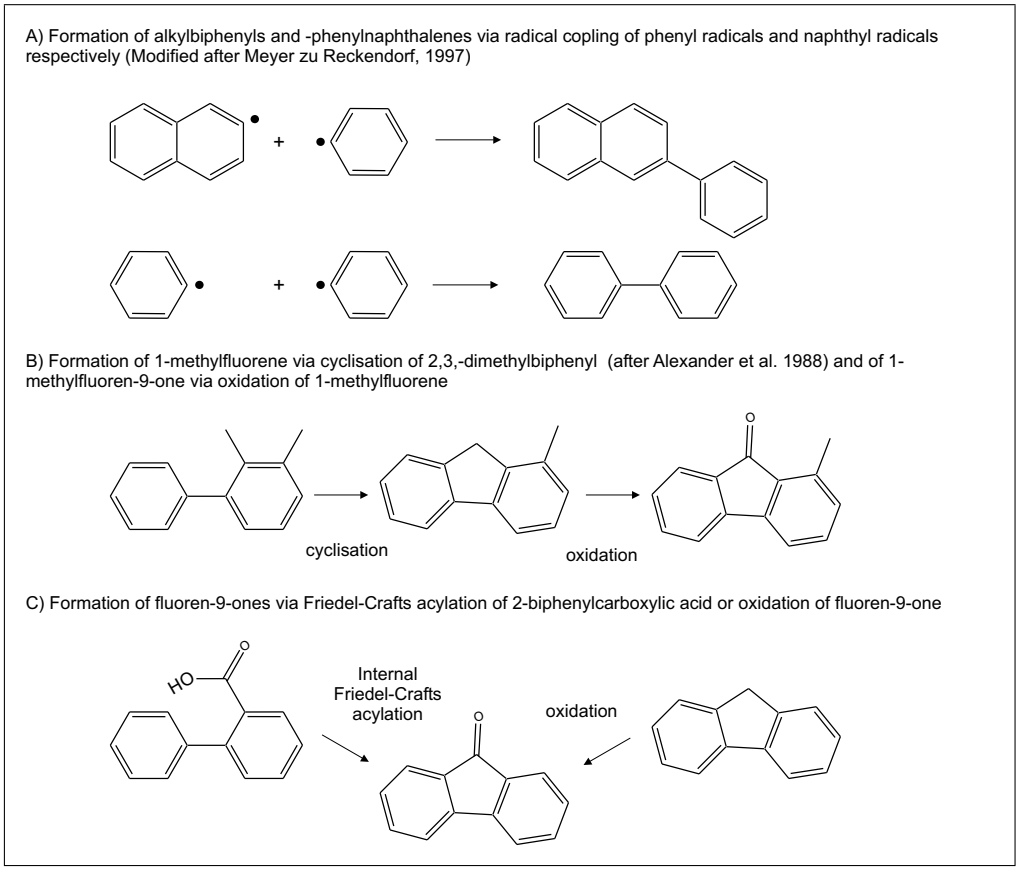

Figure 7.26: Possible formation pathways for alkylbiphenyls, -phenylnaphthalenes, -fluorenes and -fluoren-9-ones and relationships amongst these individual compound classes

alkylfluorenes, the alkylfluoren-9-ones on the other hand strongly predominate the fraction of low-polarity NSO compounds (Table 7.5).

Although they do not show the same magnitude in either the fraction of aromatic hydrocarbons and low polarity NSO compounds, the relative amounts of individual methylfluorenes and their oxygenated analogues show a strong interdependency (Fig. 7.27 A + B). This strong correlation may result from a common source for the two compound classes. However, it is more likely that the relationship results from the strong oxidation of methylfluorenes. In analogy to ethylnaphthalenes the benzylic carbon of alkylfluorenes is highly activated for oxidation. The strong correlation of naphthylketones and ethylnaphthalenes already indicated, that oxidation affected the organic matter of the North English coals. The oxidation of alkylfluoren-9-ones to carboxylic acids is not observed. In contrast to the forma-

Table 7.5: Occurrence of alkylfluorenes (Fl), alkylbiphenyls (BP), alkylphenylnaphthalenes (PN) and alkylfluoren-9-ones (Flo) in North English coals

Sample	Fl	BP	PN	Flo
E 48388	+	+	+	+++
E 48389	+	+	+	+++
E 48390	+	+	+	+++
E 48214	+	+	+	+++
E 48216	+	+	+	+++
E 48220	+	+	+	+++
E 48403	+	+	+	+++
E 48405	+	+	+	+++
E 48392	+	+	+	+++
E 48393	+	+	+	+++
E 48394	+	+	+	+++
E 48395	+	+	+	+++
E 48396	+	+	+	+++
E 48397	+	+	+	+++
E 48398	+	+	+	+++
E 48400	+	+	+	+++
E 48401	+	+	+	+++
E 48382	+	+	+	+++
E 48383	+	+	+	+++
E 48384	+	+	+	+++

+++:abundant, ++:present
+:present to low amounts

tion of alkylnaphthalenecarboxylic acids from naphthylketones or alkylnaphthaldehydes, the analogue reaction for alkylfluoren-9-ones would result in the breakdown of the tricyclic ring system.

The distribution of methylfluorenes and -fluoren-9-ones for individual samples of the North English coals does not differ significantly and shows no dependence on maturity. Especially the strong correlation for 1-methylfluorene/-fluoren-9-one (Fig. 7.27 A) results from the fact, that these two compounds have generally been the most abundant isomers of methylfluorenes and -fluoren-9-ones, respectively. Although no maturity dependence for individual isomers is found, the compounds generally show a strong correlation to 2- and 3-methylphenanthrene but also 2,6- and 2,7-dimethylphenanthrene. The two compound classes therefore reveal an enhanced thermal stability. The good correlation to thermodynamically

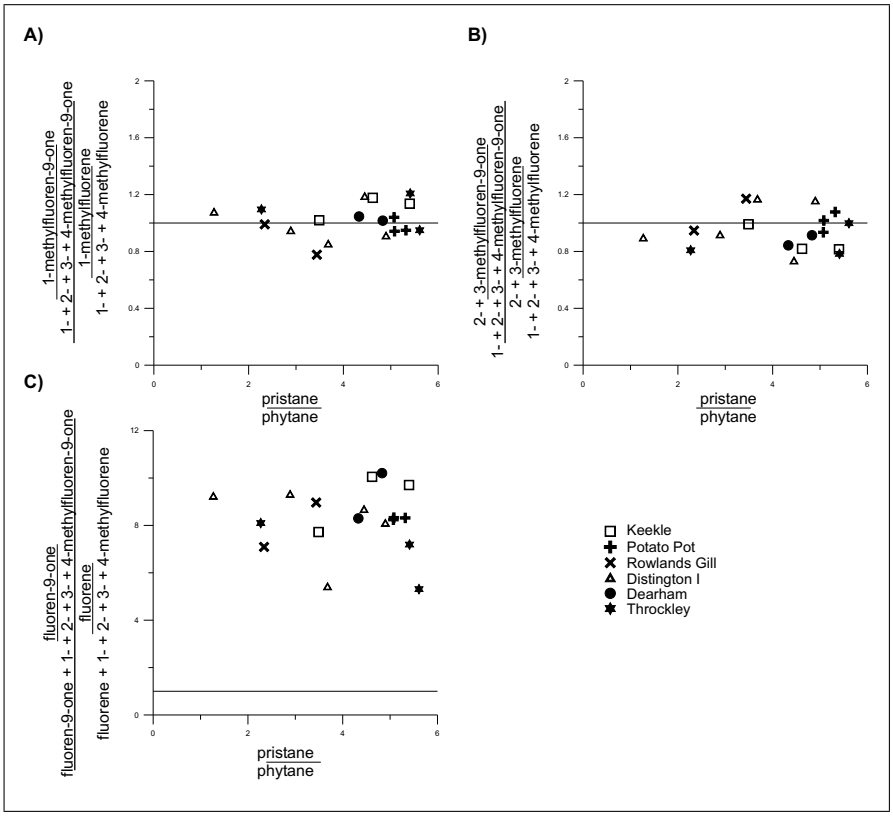

Figure 7.27: Cross plots A) and B) showing the strong correlation of methylfluorenes and -fluoren-9-ones in relation to summed isomers *vs.* the ratio of pristane/phytane and C) the high amounts of fluoren-9-one in comparison to fluorene based on summed C_{0-1}-fluoren-9-ones and fluorenes respectively *vs.* the ratio of pristane/phytane

stable alkylphenanthrenes, and the fact that the composition of methylfluorenes and -fluoren-9-ones show no significant variations indicate, that alkylfluorenes and -fluoren-9-ones lack a significant biological precursor. However this may also be due to the fact that for the maturity level of the North English coals, both formation and isomerisation of alkylfluorenes and -fluoren-9-ones are insignificant. The relative amounts of the compounds do not depend on the redox potential of the depositional environment. This indeed may be explained by a random formation at very early stages of sedimentation.

Although the amounts of fluorene in relation to fluoren-9-one do not correlate to the amounts of the corresponding methylated analogues (Fig. 7.27 C), this probably is not due to biodegradation (Fig. 6.34). Biodegradation is supposed to play a minor role for the North English coals. It has been discussed previously, that the

composition of aliphatic and aromatic hydrocarbons for this subset does not indicate intensive biodegradation. While fluoren-9-ol was generally abundant in the medium-polarity NSO compound fraction, the corresponding methylfluoren-9-ols were absent. Actually it is unlikely that fluorene has been strongly biodegraded while this should not have been the case for methylfluorenes or other compounds. A preferential oxidation of the unsubstituted compound is not likely. The fact, that the relative amounts of fluoren-9-one in comparison to fluorene do not depend on the ratio of pristane/phytane and scatter around eight (Fig. 7.27 C) for all North English coals indicates, that either fluorene and its oxygenated analogue originate from different sources or are formed via a pathway deviating from that of the corresponding methylated homologues. Neither volatilisation (bp of fluorene: 295°C) nor an enhanced susceptibility to oxidation may account for the strongly different behaviour of the unsubstituted compounds. The elevated amounts of fluoren-9-one might be due to an elevated formation via cyclisation of 2-biphenylcarboxylic acid. This however is improbable. Although 2-biphenylcarboxylic acid in contrast to 3- and 4-biphenylcarboxylic acid was absent in either of the North English coals, the latter two carboxylic acids have only been trace compounds in the acid fraction of some samples. Although these findings, strongly indicate a loss of 2-biphenylcarboxylic acid due to intramolecular Friedel-Crafts acylation, this is supposed to play a minor role, due to the low amounts of 3- and 4-biphenylcarboxylic acids and the absence of methylated homologues in general. The findings may be explained by two other hypotheses. Fluoren-9-one, contrary to methylfluoren-9-ones may have an additional, yet unknown source. However it may also be possible that high amounts of fluorene have been present in the sediments much earlier than the corresponding methylfluorenes. These amounts of fluorene then could have been oxygenated prior to the formation of methylfluorenes. Both hypotheses explain the high amounts of fluoren-9-one in comparison to fluorene.

Although it has been suggested, that alkylbiphenyls and -phenylnaphthalenes are formed via radical coupling, their amounts show no correlation (Fig. 7.28). This indicates, that the two compound classes are either formed via different pathways or that they do have a more specific precursor strongly influencing their relative amounts. A similar formation pathway is expected to result in correlation between the two groups. Alkylbiphenyls generally are minor contributors to the fraction of

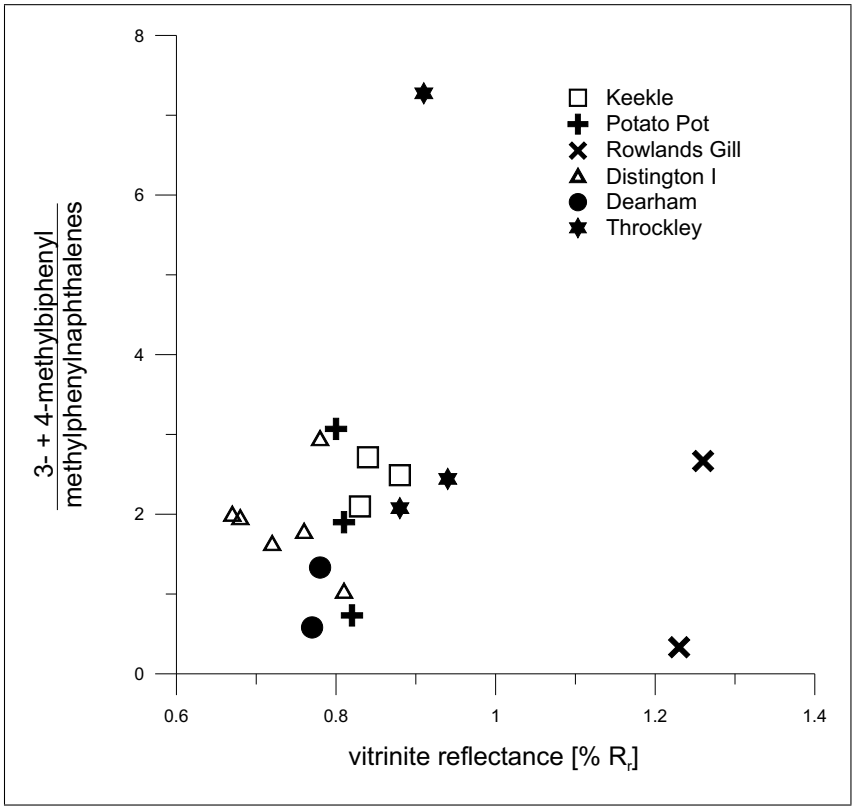

Figure 7.28: Plot indicating that neither the relative amounts of alkylbiphenyls to alkylphenylnaphthalenes increase with increasing maturity nor that they stay constant

aromatic hydrocarbons and normally show no dependency on other compounds. It therefore is suggested, that they are formed randomly and do not possess a specific precursor.

In contrast amounts of alkyl-2-phenylnaphthalenes correspond to 2- and 3-methylphenanthrene, 2,6- and 2,7-dimethylphenanthrene and to alkylfluorenes. This however does not indicate a biogenic precursor but points to an enhanced thermal stability of $C_{(0-1)}$-2-phenylnaphthalenes. Additionally neither for the specific alkylphenanthrenes nor for alkylfluorenes in general a specific precursor was indicated. The correlation due to thermal stability in contrast is well-founded by the fact that especially alkyl-2-phenylnaphthalenes in comparison to 1-phenylnaphthalenes are characterised by an enhanced thermal stability.

7.3.2 Group II

While alkylnaphthalenes and -phenanthrenes were abundant in the six immature coals, this does not account for alkylfluorenes, -biphenyls and -phenylnaphthalenes in general (Table 7.6). Alkylfluoren-9-ones in contrast were highly abundant in all six samples (Table 7.6). For the biodegraded coal from the Moscow Basin, none of the three compound classes of aromatic hydrocarbons was detected, this again may be due to biodegradation. The two German coals only lack the presence of alkylbiphenyls (Table 7.6). The compounds were generally not abundant in the Upper Viséan coal, while few isomers were detected in the Westphalian D coal.

Table 7.6: Occurrence of alkylfluorenes (Fl), alkylbiphenyls (BP), alkylphenylnaphthalenes (PN) and alkylfluoren-9-ones (Flo) in immature type III samples

Sample	Fl	BP	PN	Flo
E 49710	+	+	+	+++
E 48996	+	+/-	+	+++
E 48988	-	-	-	+++
E 48989	+	+	+	+++
E 48993	+	-	+	+++
E 48991	+	+	+	+++

+++:abundant, +:present to low amounts, -:absent, +/-: few isomers present

Methylfluorenes and fluoren-9-ones in contrast to the North English coals show weak correlation for the five coals of low maturity where both compounds have been present (Fig. 7.29 A-C). This is most pronounced for the Upper Viséan coal from Germany, where composition of methylfluoren-9-ones, instead of 1-methylfluoren-9-one is strongly dominated by 2- and 3-methylfluoren-9-one. Additionally this sample shows a significantly depleted proportion of fluoren-9-one (Fig. 7.29 C).

It is improbable that the oxidation of methylfluorenes is controlled kinetically. The Upper Viséan coal from Germany would be the only sample affected by a kinetically control (Fig. 7.29 A-B). The suggestion that methylfluorenes and -fluoren-9-ones do not completely originate from the same source, and that the

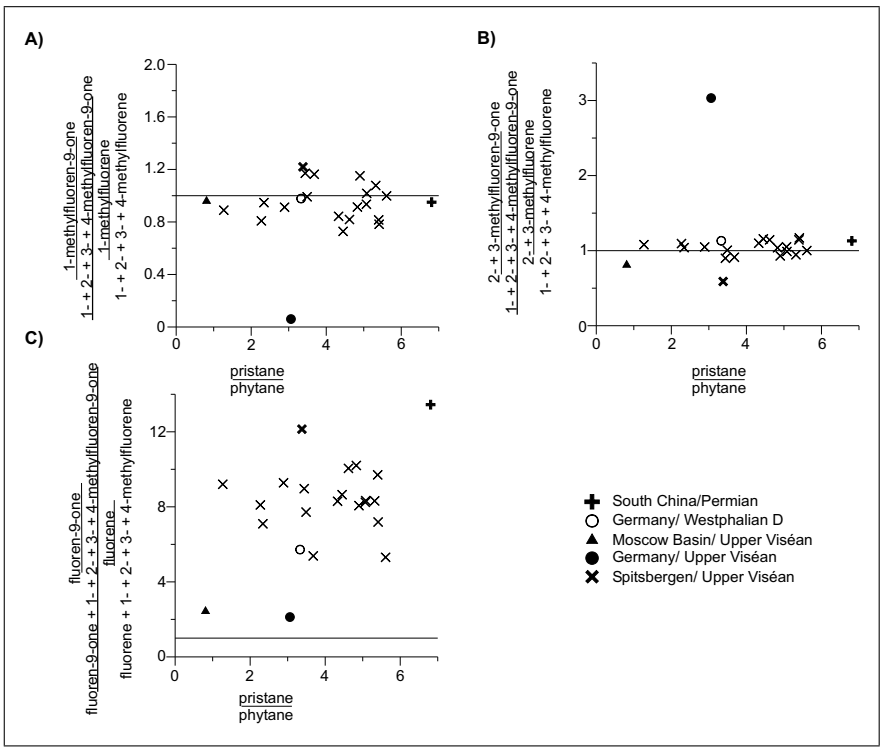

Figure 7.29: Cross plots A) and B) showing the weaker correlation of methylfluorenes and -fluoren-9-ones in relation to summed isomers *vs.* the ratio of pristane/phytane and C) the normally high amounts of fluoren-9-one in comparison to fluorene based on summed C_{0-1}-fluoren-9-ones and fluorenes respectively *vs.* the ratio of pristane/phytane

deviations especially for methylfluoren-9-ones in the Upper Viséan coal represent a more natural distribution therefore is more likely. 1-Methylfluoren-9-one probably is the most stable isomer of methylfluoren-9-ones and therefore normally is the most abundant isomer for the majority of the investigated samples. In analogy to the North English coals, an enhanced formation of individual methylfluoren-9-ones from 2-biphenyl carboxylic acids however can be ruled out, due to none of the six samples showing the presence of carboxylic acids based on the biphenyl skeleton.

The absence of biphenylcarboxylic acids in the immature samples may additionally support the hypothesis that carboxylic acids, besides biodegradation are formed via abiotic oxidation at elevated temperatures, only.

The strong differences for the relative amounts of fluorene and fluoren-9-one in the immature samples are in analogy to the findings for the North English coals. However, the six immature samples show stronger variations (Fig. 7.29 C). This again supports the hypothesis, that fluorene and fluoren-9-one are partly formed via other pathways than the corresponding methylfluorenens and -fluoren-9-ones. The strong correlation of fluorene to compounds like naphthalene, 1- and 2-methylnaphthalene, 1,2,7-trimethylnaphthalene, cadalene, or phenanthrene points to its weak thermal stability. This corresponds to the hypothesis that low substituted compounds are subject to methylation at low maturity ranges, while demethylation may result from enhanced thermal stress at elevated maturities. The relatively low amounts of fluorene in comparison to fluoren-9-one for the immature samples therefore may be due to methylation reactions preferentially affecting the aromatic hydrocarbon.

Methylfluorenes for the immature samples show a slight correlation to diphenylmethane. This may indicate, that they are formed from diphenylmethane derivatives via radically induced cyclisation. However, besides the fact that the correlation is not to strong, the low maturities of the samples contradict an advanced formation of radically formed compounds.

According biogenic relationships, especially 4-methylfluorene is characterised by a strong correlation to ip-iHMN and retene. This in correspondence to the observed biogenic relationships for alkylnaphthalenes and -phenanthrenes may indicate a common origin of these compounds. Although a formation of 4-methylfluorene from precursors of ip-iHMN and retene is improbable, the compound might originate from another biogenic precursor strongly corresponding to phyllocladane and similar diterpenes. Based on the observations for the North English coals, where alkylfluorenes showed strong correlations to stable isomers of alkylphenanthrenes, it was proposed that the compounds are characterised by an enhanced thermal stability. Correlations between alkylfluorenes and stable isomers of alkylphenanthrenes are not observed for the immature coals. However it should be recognised, that these individual alkylphenanthrenes for the six immature coals showed no dependence on maturity. In contrast for the six immature samples alkylfluorenes are characterised by a good correlation to tetramethylnaphthalenes. For the six coals,

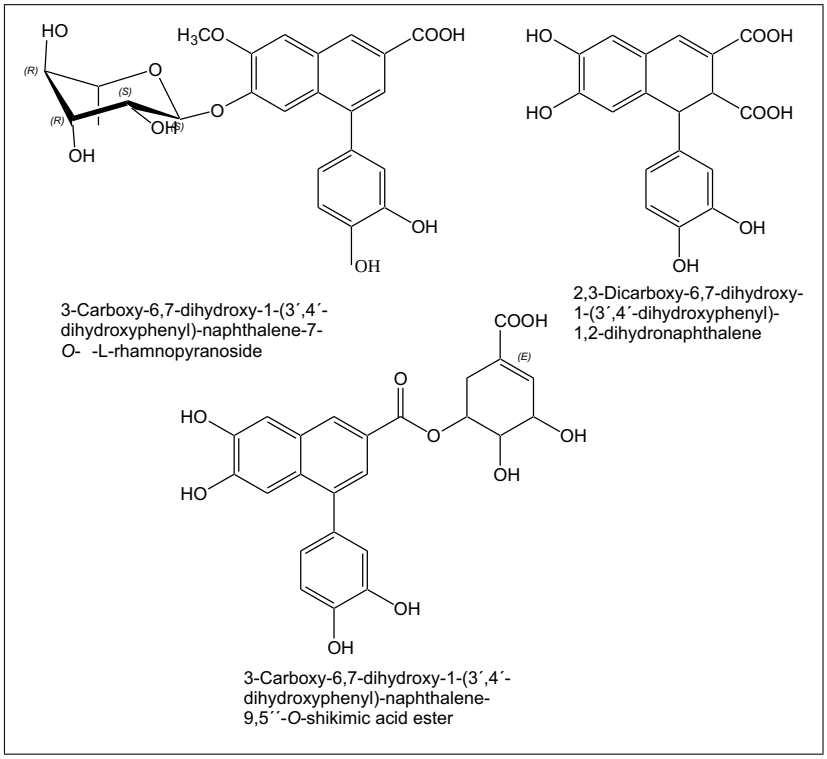

Figure 7.30: Possible biogenic precursors of alkylphenylnaphthalenes present in liverworts (Cullmann *et al.*, 1999)

a relative increase of these compounds with maturity has been observed. Therefore the findings support the hypothesis, that relative amounts of alkylfluorenes increase with increasing maturity.

The absence of almost all alkylbiphenyl isomers in the two German coals is striking, as these are the two samples showing the strongest terrigenous contribution and the weakest alteration of organic matter. This indeed indicates, that alkylbiphenyls are formed randomly and have no direct biogenic precursors. Due to the absence of alkylbiphenyls accompanied by the presence of alkyl-2-phenylnaphthalenes it is improbable that the two compound classes are formed via similar pathways or share a precursor. It can be assumed, that alkylbiphenyls do not originate from the coupling of lignin derived compounds but at least at low maturities lack a direct potential natural precursor. Additionally their absence accompanied by the presence of alkylfluorenes in the two German coals, indicates that cyclisation reactions of *ortho*-substituted alkylbiphenyls are not the

only possible precursors of alkylfluorenes. Besides these facts, in analogy to the observations for the North English coals, distributions of alkylbiphenyl reveal little information.

This does not account for the 2-phenylnaphthalenes. In agreement to the distribution in North English coals, alkylfluorenes and alkyl-2-phenylnaphthalenes are characterised by a weaker but still good correlation. This may point to the hypothesis, that the respective precursors of these compounds are related or transformed at the same level of thermal stress or that the compounds themselves show a comparable thermal stability. Alkylphenylnaphthalenes, in contrast to alkylbiphenyls but also alkylfluorenes indeed may have direct natural precursors. Several lignans (Cullmann *et al.*, 1999; Davin and Lewis, 2000) possess a structure based on the 1-phenylnaphthalene skeleton (Fig. 7.30). These lignans are present in liverworts (Cullmann *et al.*, 1999), which have been suggested to be precursors of early land plants (Qiu *et al.*, 1998). 2-Phenylnaphthalenes may be formed from 1-phenylnaphthalenes via isomerisation reactions at low maturities. 2-Phenylnaphthalenes due to the depleted sterical hinderance probably are characterised by an elevated thermal stability. This may hold for the good correlation of these compounds to alkylfluorenes.

7.3.3 Group III

For the mature type II-III sediments, alkylfluorenes are not generally abundant (Table 7.7). Their absence in two of the samples from East Greenland may be due to their weak proportions of TOC. Alkylbiphenyls in contrast were only present in the Russian sample in general (Table 7.7). While they have been absent in the two fossils, the samples from East Greenland are characterised by the presence of few isomers, only. Alkylfluoren-9-ones, in analogy to previously discussed samples, were generally highly abundant (Table 7.7).

Table 7.7: Occurrence of alkylfluorenes (Fl), alkylbiphenyls (BP), alkylphenylnaphthalenes (PN) and alkylfluoren-9-ones (Flo) in mature type II-III samples

Sample	Fl	BP	PN	Flo
E 49748	+	-/+	+	+++
E 49749	-	-/+	+	+++
E 49750	-	-/+	+	+++
E 49751	+	-/+	+	+++
E 48990	+	+	+	+++
E 48430	+	-	+	+++
E 48425	+	-	+	+++

+++:abundant, +:present to low amounts, -/+:few isomers present, -:absent

The distribution of methylfluorenes to -fluoren-9-ones for the mature samples support the hypothesis, that the latter compounds are formed from the former compounds via abiotic oxidation. These hypothesis is based on the observations for the North English coals and the immature coals. The good correlations are least pronounced for the most mature sample, the *Mesocalamites cf. Taitianus*, which for this subset of samples has been the one characterised by the lowest ratio of pristane/phytane. However for other samples no dependence on the redox potential of the sediments has been observed. In agreement to former observations the relative amounts of individual isomers are influenced by their thermal stabilities while influences of biogenic precursors are not recognisable. The relative amounts of fluorene in relation to methylfluorenes corresponds to the findings for the North English coals. Due to the strong differences between the relative amounts of flu-

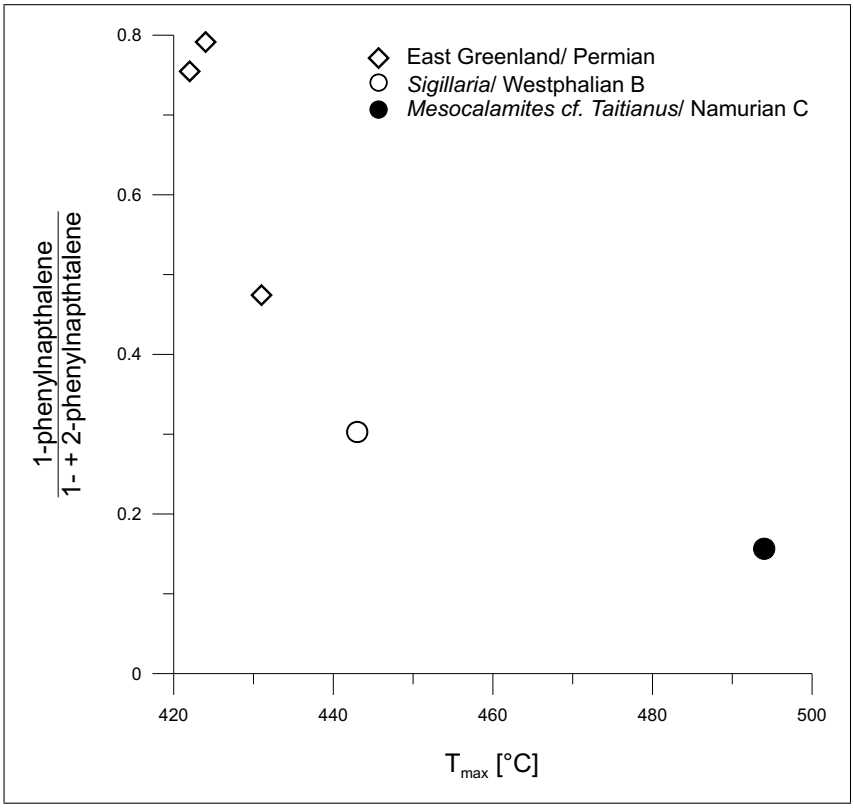

Figure 7.31: Cross plot displaying the ratio of 1-phenylnaphthalene/1- and 2-phenylnaphthalene *vs.* T_{max}

orene and fluoren-9-one it has been suggested previously in this thesis that the formation of fluoren-9-one differs to the one of methylfluoren-9-ones.

Based on the observations for the North English coals and the immature coals it has previously been suggested that at least the relative amounts of $C_{(0-1)}$-2-phenylnaphthalenes and -fluorenes increase with increasing thermal maturity. In analogy to the former discussed subsets, alkylfluorenes and -2-phenylnaphthalenes are characterised by a good correlation. However, this correlation is less pronounced than for the North English coals. Additionally neither $C_{(0-1)}$-fluorenes nor $C_{(0-1)}$-2-phenylnaphthalenes show a strong correlation to the stable isomers of methylphenanthrenes and dimethylphenanthrenes. This corresponds to the observations made for the immature coals. In analogy alkylphenanthrenes for the mature samples showed weak correlation to vitrinite reflectance. Individual alkylfluorenes and -2-phenylnaphthalenes in contrast are characterised by a pos-

itive correlation to T_{max}. This to some extend points to an enhanced thermal stability of the compounds. It should be recognised that for this subset of samples T_{max} sometimes proofed to be a better maturity parameter than vitrinite reflectance.

Due to the aromatic hydrocarbon standard not being added to six of the seven samples a direct comparison between the relative amounts of 1-phenylnaphthalene and 2-phenylnaphthalene was carried out. While correlation to vitrinite reflectance was less pronounced, 1-phenylnaphthalene shows a relative decrease with increasing T_{max} (Fig. 7.31). Marynowski *et al.* (2001) found a relative decrease of 1-phenylnaphthalene with increasing vitrinite reflectance. The correlation for the six samples to T_{max} refers to this observation. It has been stated previously, that correlation to both vitrinite reflectance and T_{max} has not been very strong, while for example correlation of individual alkylnaphthalenes to T_{max} has been relatively enhanced.

The relative depletion of 1-phenylnaphthalene may account for the natural precursor of this compound. Due to thermal maturation, alkyl-1-phenylnaphthalenes are easily converted into the more stable alkyl-2-phenylnaphthalene.

The absence of several alkylbiphenyls in many of the samples in contrast may account for a depleted thermal stability of these compounds.

7.3.4 Group IV

While $C_{(0-1)}$-fluorenes and $C_{(0-1)}$-2-phenylnaphthalenes normally were abundant in the type I samples, this again does not account for alkylbiphenyls (Table 7.8). This again supports the hypothesis that the formation of alkylphenylnaphthalenes and -biphenyls does not depend.

Table 7.8: Occurrence of alkylfluorenes (Fl), alkylbiphenyls (BP), alkylphenylnaphthalenes (PN) and alkylfluoren-9-ones (Flo) in immature type I organic matter

Sample	Fl	BP	PN	Flo
E 48478	+	-	+	+++
E 48479	+	-	+	+++
E 48480	-	+	-	+++
E 48985	+	+	+	+++
E 48986	+	+	+	+++
E 48987	+	+	+	+++
E 48992	+	+	+	-

+++:abundant, +:present to low amounts, -:absent

Alkylfluoren-9-ones were detected in all of the samples except for the Devonian sample from Spitsbergen (Table 7.8). This sample is not characterised by a weak low-polarity NSO compound fraction. However, it is unlikely that the absence of alkylfluoren-9-ones but presence of alkylfluorenes indicates an age specific characteristic. This is well-founded by the fact, that relative amounts of methylfluorenes and -fluoren-9-ones for the majority of the investigated samples were characterised by strong correlations. It is most likely that the absence of alkylfluoren-9-ones in the sample from Spitsbergen is due to a depositional environment preventing the oxidation of alkylfluorenes. Nevertheless the absence of alkylfluoren-9-ones is significant due to the presence of both, alkylnaphthaldehydes and -naphthylketones in this sample. It has been suggested in this thesis that the oxidation of alkylnaphthalenes and -fluorenes proceeds easily. The fluorene skeleton is characterised by an even more activated benzylic carbon and the absence of alkylfluoren-9-ones therefore is remarkable.

For the other type I samples the 1-methyl isomer of both compound classes generally is the most abundant and the 4-methyl isomer the least abundant. These findings indicate, that the distribution for the type I samples as for the type II-III organic matter is not significantly influenced by a contribution from specific sources. In contrast to the low maturity type II-III samples, fluorene in comparison to methylfluorenes is present in constant amounts.

The strong correlation between alkylfluorenes and 2- and 3-methylphenanthrenes and 2,6- and 2,7-dimethylphenanthrenes observed for the North English coals is also found for the type I samples. Although alkylphenanthrenes for these latter samples showed no dependence on maturity, the analogies indicate, that the thermal stability of alkylfluorenes and more stable alkylphenanthrenes correlate. This refers to the hypothesis of van Aarssen *et al.* (2001), that liquid phase reactions affect mobile compounds to same amounts. A contribution of the compounds at the maturity level of the immature type I samples therefore is excluded as it would affect the composition of the mobile phase like has been observed for the immature type II-III samples.

In contrast to previously discussed samples, alkylfluorenes and -2-phenylnaphthalenes except for one C_1-2-phenylnaphthalene show weak correlation. Additionally $C_{(0-1)}$-2-phenylnaphthalenes show a weak dependence on vitrinite reflectance. The weak correlation does also account for individual isomers of $C_{(0-1)}$-2-phenylnaphthalenes. However 2-phenylnaphthalene and the last two eluting C_1-2-phenylnaphthalenes often are characterised by a strong correlation to alkylphenanthrenes. These findings indicate that for type I organic matter different sources of alkyl-2-phenylnaphthalenes are recognisable while for terrigenous organic matter the contribution from a general precursor are predominant.

Again, like for all previously discussed samples, alkylbiphenyls reveal negligible information.

7.4 Heterocyclic Compounds: Formation Via Unspecific Pathways or from Biogenic Precursors?

7.4.1 Group I

Alkyldibenzothiophenes, -carbazoles, -dibenzofurans, benzo[*b*]naphthofurans and alkylxanthones share in common, that they incorporate a hetero-atom in the ring system. For their detection in the North English coals see Table 7.9. While alkyldibenzothiophenes have been subject to intensive studies in the past, investigations about the origin and formation pathway of the other compound classes have only started lately. Although an unambiguous source for neither of the compound classes is known, their formation pathways are supposed to differ. They may have either direct natural precursors or may be formed randomly in sediments. The latter origin at least for alkyldibenzothiophenes, the compounds that attracted most interest, is generally accepted.

The amounts of alkyldibenzothiophenes are suggested to depend on the thermal maturity and the availability of reduced sulphur i.e. the origin and depositional environment of organic matter. Although it has been mentioned previously, that the two most mature samples of the North English coals indeed are characterised by elevated amounts of alkyldibenzothiophenes, this does also account for an immature sample from Distington (Fig. 7.32 B). For these three samples high amounts of alkyldibenzothiophenes additionally correlate to their enhanced proportions of total sulphur (Fig. 7.32 A). The availability of reduced sulphur in early stages of diagenesis should correspond to low ratios of pristane/phytane. Many of the North English coals characterised by high proportions of total sulphur additionally show low ratios of pristane/phytane (Fig. 7.32 B). It is presumable that the precursors of alkyldibenzothiophenes are formed during early stages of diagenesis in a reducing environment. The formation of alkyldibenzothiophenes however probably occurs later at elevated maturity levels. This at least may hold for the strong variations for the relative amounts of methyldibenzothiophenes in compar-

Table 7.9: Occurrence of alkyldibenzothiophenes (DBT), -carbazoles (C), -dibenzofurans (DBF), benzo[*b*]naphthofurans (BNF) and -xanthones (X) in North English coals

Sample	DBT	C	DBF	BNF	X
E 48388	+	+	++	+	+
E 48389	+	+	++	+	+
E 48390	+	+	++	+	+
E 48214	+	+	++	+	+
E 48216	+	+	++	+	-
E 48220	+	+	++	+	+
E 48403	+	+	++	+	-
E 48405	+	+	++	+	-
E 48392	+	+	++	+	-
E 48393	+	+	++	+	+
E 48394	+	+	++	+	+
E 48395	+	+	++	+	-
E 48396	+	n.d.	++	+	-
E 48397	+	+	++	+	-
E 48398	+	+	++	+	+
E 48400	+	+	++	+	+
E 48401	+	+	++	+	+
E 48382	+	+	++	+	-
E 48383	+	+	++	+	-
E 48384	+	+	++	+	-

++:present, +:present to low amounts,
-:absent, n.d.:not determined

ison to the depositional environments reflected by the amounts of total sulphur and the ratio of pristane/phytane (Fig. 7.32). However it does not explain the high amounts of alkyldibenzothiophenes for the relatively immature sample from Distington.

None of the individual methyldibenzothiophenes and none of the maturity parameters based on alkyldibenzothiophenes (Fig. 7.3 C) is characterised by a strong correlation to maturity. Nevertheless summed methyldibenzothiophenes for North English coals are characterised by a strong correlation to summed methylfluorenes and -2-phenylnaphthalenes. This is most pronounced for the two coals characterised by elevated maturities. In these two samples amounts of alkylfluorenes, -2-phenylnaphthalenes and -dibenzothiophenes in comparison to alkyldibenzofurans (Fig. 7.33 A and B) are significantly enhanced. Amounts of methyldiben-

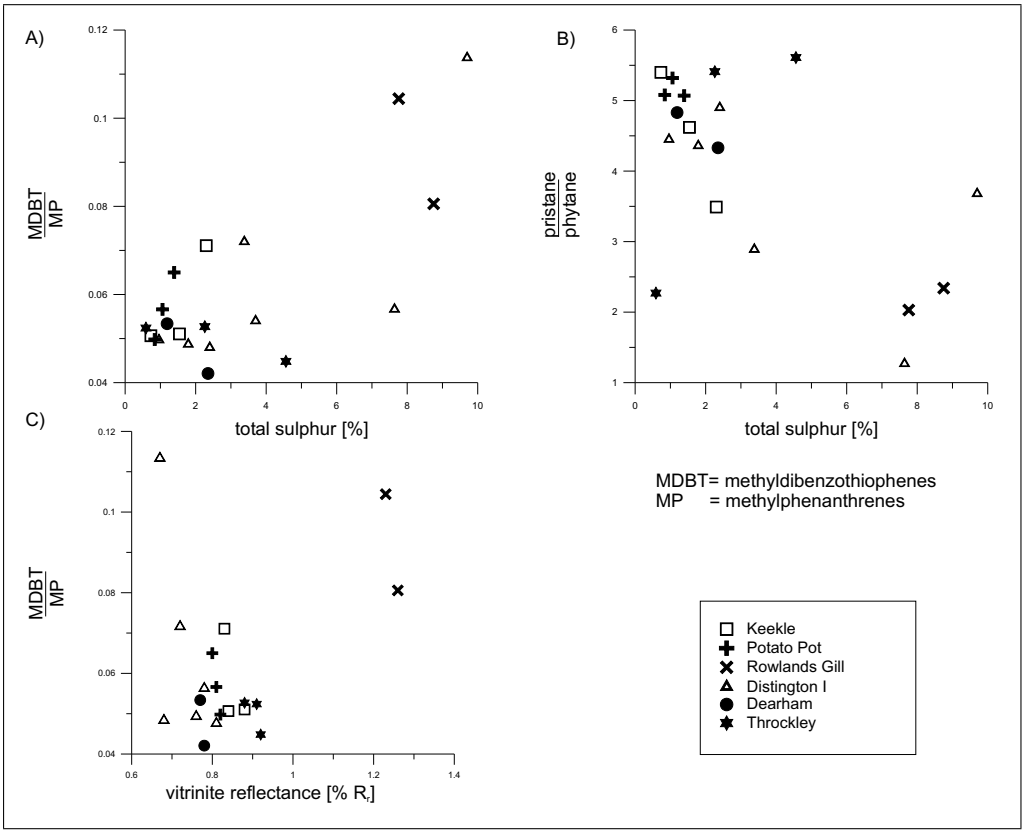

Figure 7.32: Cross plots indicating that the relative amounts of alkyldibenzothiophenes do A) slightly depend on the amounts of total sulphur, that B) the redox potential and the amounts of total sulphur to some extent correlate and C) that the relative amounts of alkyldibenzothiophenes do not exclusively depend on the maturity of the sediments

zothiophenes do also correlate to methylfluoren-9-ones. While the correlation between alkylfluorenes and alkyldibenzothiophenes can be attributed to a thermally induced formation unambiguously, the correlation to alkylfluoren-9-ones is more contradictory. Although it is most likely that the formation of alkylfluorenes and -phenylnaphthalenes is favoured in oxidising environments, the formation of alkylfluoren-9-ones in the North English coals is supposed to require oxic conditions. This is well-founded by the fact, that Friedel-Crafts acylation of alkyl-2-biphenylcarboxylic acids is a minor source of alkylfluoren-9-ones. It therefore is assumable, that the presence of reduced sulphur may be an important factor at early stages of deposition only, when precursors of alkyldibenzothiophenes are formed. In contrast maturity is more important according the summed amounts of alkyldibenzothiophenes and to some degree perhaps also the relative

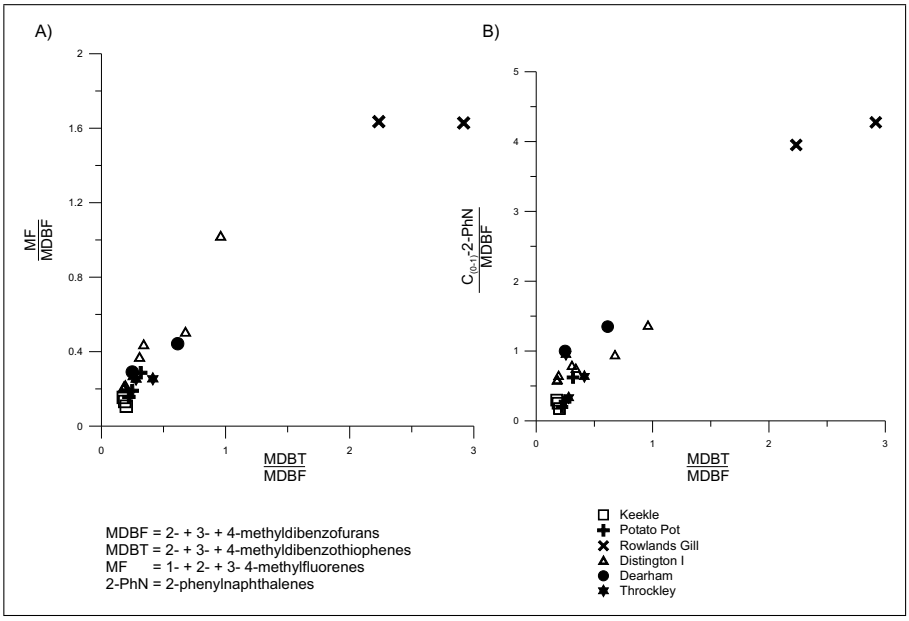

Figure 7.33: Cross plots indicating a strong correlation between the amounts of A) methylfluorene/methyldibenzofurans and B) $C_{(0-1)}$-phenylnaphthalenes/methyldibenzofurans *vs.* methyldibenzothiophenes/methyldibenzofurans

amounts of individual isomers. This indeed explains the good correlation between alkyldibenzothiophenes and -2-phenylnaphthalenes. It was suggested in this thesis that the precursors of alkyl-2-phenylnaphthalenes i.e. defunctionalised alkyl-1-phenylnaphthalenes are released at early stages and that transphenylation occurs due to the raise of thermal maturity.

Although it has been suggested earlier in this thesis, that alkylcarbazoles, by analogy to alkyldibenzothiophenes, are formed due to the presence of reduced nitrogen, the two compound classes do not correlate. The high proportions of alkylcarbazoles in samples showing elevated ratios of pristane/phytane indicates that their formation does not strongly depend on the availability of reduced nitrogen at early stages of diagenesis. Additionally relative amounts of summed alkylcarbazoles, contrary to the amounts of summed alkyldibenzothiophenes, show no dependence on maturity. The only exception is that higher homologues deplete at enhanced maturities. This has already been observed for alkylnaphthalenes and is controlled thermally. For North English coals, except for the mature type III coal, variations in the relative amounts of methylcarbazoles are weak. This indicates

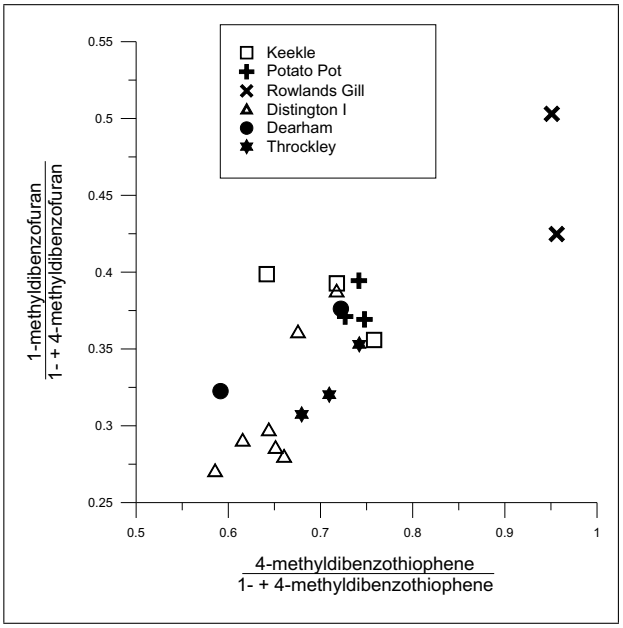

Figure 7.34: Cross plot indicating that the ratios of 1-methyldibenzofuran/1- + 4-methyldibenzofuran *vs.* 4-methyldibenzothiophene/1- + 4-methyldibenzothiophene show a strongly positive correlation while due to the thermodynamic stability of the isomers the correlation is supposed to be negative

that within the maturity range of the North English coals, isomerisation reactions of alkylcarbazoles are negligible. Additionally it can be presumed that in analogy to many of the previously discussed compound classes, contribution of individual isomers from a specific source does not influence the composition of this compound class at the present maturity level. Although it is supposed above that the formation of alkylcarbazoles does not strongly correlate to the availability of reduced nitrogen at early stages of diagenesis, an early formation may explain the strong homogeneity in distribution of individual isomers for alkylcarbazoles. The distribution of individual isomers for alkylfluorenes, -fluoren-9-ones and -carbazoles is similar, with the 1-methyl isomer being predominant and 4-methyl isomer being the leanest. Nevertheless correlation between the three compound classes for the North English coals is weak. This strongly indicates, that although alkylcarbazoles have no specific source, the relative thermal stabilities of individual isomers do not strongly correspond to the analogue compounds based on the fluorene or fluoren-9-one skeleton.

For alkyldibenzofurans an origin from terrestrial sources has been suggested (Radke *et al.*, 2000). The high amounts of these compounds in the North English coals support this hypothesis. In contrast to for example alkylcarbazoles, individual isomers of alkyldibenzofurans show strong variations for the North En-

glish coals. Correlations between alkyldibenzofurans are less pronounced than for alkyldibenzothiophenes and -naphthalenes. The sixth eluting C_2-dibenzofuran for example is the only one showing a relative increase with increasing vitrinite reflectance. In contrast 3-methyldibenzofuran, the two ethyldibenzofurans and the last eluting dimethyldibenzofuran show a relative decrease with increasing vitrinite reflectance and a strong correlation to each other. The weak correlation for individual isomers of alkyldibenzofurans in correspondence to the hypothesis made for alkylphenanthrenes and -naphthalenes indicates, that the distribution of this compound class for the North English coals is strongly influenced by the contribution from specific sources for distinct isomers.

Especially 1-methyldibenzofuran is the compound showing weakest correlation at all. This supports the hypothesis, that it originates from a specific source, i.e. constituents of lichens (Radke *et al.*, 2000). Although 1-methyldibenzofuran shows no unambiguous increase with increasing vitrinite reflectance for North English coals, its relative amounts in comparison to 4-methyldibenzofuran strongly differ to the corresponding isomers of methyldibenzothiophenes (Fig. 7.34). This is in clear contrast to the similarity in thermodynamic stability for methyldibenzofurans and -thiophenes.

Although benzo[*b*]naphthofurans and alkyldibenzofurans are related in magnitude of amounts, individual isomers of the two compound classes show no enhanced correlation. Variations for the four benzo[*b*]naphthofurans are weak, and do not depend on vitrinite reflectance, except for the fact that benzo[*b*]naphtho[*1,2-d*]furan and benzo[*b*]naphtho[*2,1-d*]furan are significantly depleted in the two mature samples from Rowlands Gill. The good correlation between the four isomers indicates, that they originate from the same source. A strong correlation for all four compounds is found to the first eluting C_1-2-phenylnaphthalene. This may indicate a biogenic relationship while precursors are unknown.

The distribution of xanthone and methylxanthones is of little significance. For North English coals, they are present in samples within the maturity range of 0.67-0.88% R_r, which are characterised by enhanced proportions of pristane, generally indicating a terrestrial origin of organic matter and oxic depositional conditions.

The compounds are characterised by an elevated correlation, indicating that their formation pathway corresponds. A potential source is not indicated.

7.4.2 Group II

While alkyldibenzothiophenes, -carbazoles, -dibenzofurans, benzo[*b*]naphthofurans and alkylxanthones were abundant in the extractable organic matter of North English coals, this does not account for the low maturity type II-III coals in general. Alkyldibenzofurans and benzo[*b*]naphthofurans, except for the two ethyldibenzofurans were generally detected in all six samples (Table 7.10). In contrast alkyldibenzothiophenes were absent in the two German coals and the more mature sample from the Moscow Basin (Table 7.10). Alkylcarbazoles were not detected in the Upper Viséan coal from Germany and in the low maturity sample from the Moscow Basin (Table 7.10). Alkylxanthones were not abundant in both samples from the Moscow Basin (Table 7.10).

The most pronounced difference for alkyldibenzothiophenes in comparison to the North English coals is, that for the immature type II-III samples, they strongly correlate to alkylbiphenyls. This results from the fact, that the compound classes were absent in the same samples i.e. the two German coals. For the North English coals the formation of alkyldibenzothiophenes was supposed to be controlled by the earlier formation of precursors under reducing conditions at early stages of diagenesis. The absence of alkyldibenzothiophenes for the two samples correlates to their low amounts of total sulphur (Table A.1) and may indicate, that the precursors of alkyldibenzothiophenes have not been formed. The absence of almost all alkylbiphenyls in both samples would mean that their formation depends on certain precursors or environmental conditions not generally present in terrestrial organic matter. The observations are significant due to the fact that the two German coals were characterised by a strongly biogenic terrestrial composition of organic matter. The absence of both alkyldibenzothiophenes and most of the alkylbiphenyls indicate that the formation pathway of the compounds may interdepend (Fig. 7.35).

Although the biodegraded coal from the Moscow Basin shows enhanced proportions of total sulphur it lacks the presence of alkyldibenzothiophenes. The sample, according to its ratios of pristane/phytane and CPI_{HC} has been deposited under reducing conditions, where reduced sulphur should be available. In contrast

Table 7.10: Occurrence of alkyldibenzothiophenes (DBT), -carbazoles (C), -dibenzofurans (DBF), benzo[*b*]naphthofurans (BNF) and -xanthones (X) in immature type III organic matter

Sample	DBT	C	DBF	BNF	X
E 48988	-	+	++	++	-
E 48989	+	-	++	++	-
E 48991	+	+	++	++	+
E 48993	-	-	++	++	+
E 48996	-	+	++	++	+
E 49710	+	+	++	++	+

++:present, +:present to low amounts, -:absent

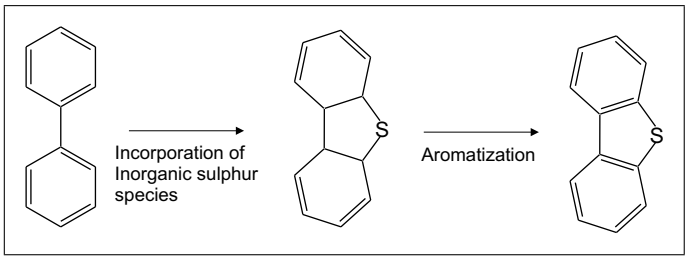

Figure 7.35: Possible diagenetic formation of alkyldibenzothiophenes from alkylbiphenyls in analogy to Sinninghe Damsté and de Leeuw (1990)

alkyldibenzothiophenes are present in the less mature sample from the Moscow Basin. This is in analogy to the observations made for the sample from Distington and shows, that maturity is not the only factor accounting for the formation of alkyldibenzothiophenes.

In contrast to the North English samples, alkyldibenzothiophenes show a weak correlation to alkylfluorenes, -fluoren-9-ones and -2-phenylnaphthalenes. This at least for alkylfluorenes and -fluoren-9-ones points to the fact that the two compound classes normally are formed at earlier stages of sedimentation than alkyldibenzothiophenes. However it may also be due to the fact that all of these compound classes are still affected by isomerisation reactions at the maturity level of the immature type II-III coals.

It has been mentioned above, that alkylcarbazoles were not detected in the immature coal from the Moscow Basin and in the Upper Viséan coal from Germany.

While their absence in the immature sample corresponds to the absence of xanthones, the German sample lacks the presence of alkyldibenzothiophenes. This does not indicate an unambiguous relationship between the compound classes. In contrast to North English coals, distributions of methylcarbazoles differ significantly. This however is in analogy to the different behaviour for alkylfluorenes and -fluoren-9-ones in the immature type II-III coals. The two least mature coals, where alkylcarbazoles were detected, in contrast to other samples show an enhanced proportion of 4-methylcarbazole. Whether this can be attributed to a specific source or to a preferential formation in sediments, which due to thermal instability is subject to kinetically induced isomerisation at low maturity levels however is unclear. Nevertheless isomers of alkylcarbazoles are characterised by a strong correlation, supporting an unspecific source of the compounds. The absence of alkylcarbazoles in two of the relative immature coals may indicate a dependence on maturity. The two samples where alkylcarbazoles were not abundant are characterised by enhanced CPI_{HC}, which indeed might indicate a dependence on maturity levels. Clegg *et al.* (1998b) found that the relative proportions of alkylcarbazoles depend on thermal maturity. The two coals show lowest pristane/phytane ratios of the subset. The hypothesis based on the observations for the North English samples, that the amounts of alkylcarbazoles do not strongly depend on the availability of reduced nitrogen at early stages of diagenesis therefore again are supported.

Although alkyldibenzofurans normally were abundant in the low maturity type II-III coals, this does not account for the two ethyldibenzofurans. They were absent in the samples of maturities below 0.6% R_r. This however is in contrast to the fact that the two compounds are of depleted thermodynamic stability and should be relatively enriched in samples of low maturities. It therefore can be suggested, that they must be formed or released from kerogen at elevated temperatures only. Contrary to its behaviour in North English coals, 1-methyldibenzofuran, is characterised by a relative increase with increasing vitrinite reflectance. For the North English coals 1-methyldibenzofuran showed no unambiguous dependence on maturity. This in correspondence to the hypothesis that 1-methyldibenzofuran originates from a specific contribution of lichens, indicates that progressive defunc-

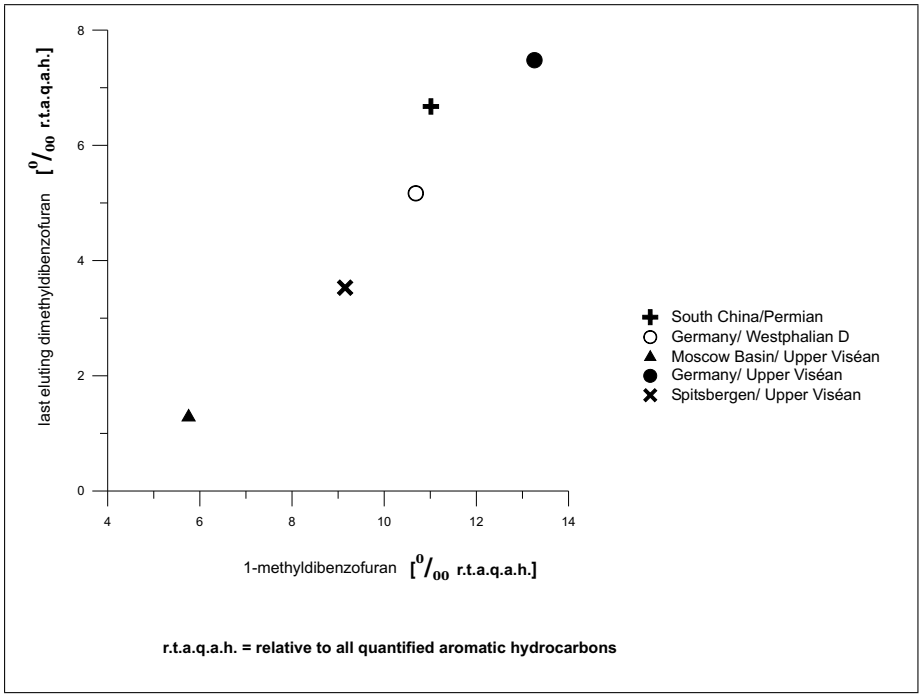

Figure 7.36: Cross plot showing the good correlation of the relative proportions of 1-methyldibenzofuran to the last eluting dimethyldibenzofuran

tionalisation of precursors at low maturities may account for the relative increase of this compound at low maturities.

At higher levels of thermal maturity the relative amounts of 1-methyldibenzofuran then should depend on the amounts of precursor released from kerogen and the magnitude of isomerisation reactions in the mobile phase. While for North English coals, especially 1-methyldibenzofuran was characterised by a weak correlation to other isomers, this for the low maturity samples does account for all methyldibenzofurans. In contrast C_2-dibenzofurans show an enhanced correlation. This does not account for the last eluting dimethyldibenzofuran, which due to its good correlation to 1-methyldibenzofuran may be characterised by a biogenic relationship (Fig. 7.36). It should additionally be recognised that this does also account for the first eluting C_1-2-phenylnaphthalene, which for North English coals showed a strong correlation to benzo[*b*]naphthofurans.

In analogy to the North English coals, benzo[*b*]naphthofurans show a strong correlation among each other. Especially for this subset of samples, where relationships

could be easily assigned this supports the hypothesis, that the compounds originate from a common source. However their general presence in all six samples strongly indicates, that their formation does not require enhanced thermal stress. This indicates a biological source, which easily condensates.

Xanthone and methylxanthones were absent in the two immature samples originating from the Moscow Basin. A formation at elevated thermal maturities may account for this. Additionally the two samples are characterised by depleted amounts of pristane corresponding to depositional environments that have not been strongly oxic. Although the compounds are characterised by a strong correlation, their relative abundances in comparison to the North English samples, varies more significantly. The two German coals show enhanced proportions of 3-methylxanthone. This may either result from the relatively low thermal maturity of the samples or from their strongly terrigenous composition. The latter fact would indicate a specific biogenic precursor of alkylxanthones.

7.4.3 Group III

For the more mature type II-III samples, alkyldibenzothiophenes and -dibenzofurans are the only low-polarity NSO compounds being generally abundant (Table 7.11). However, for the two fossils, 1-ethyldibenzothiophene, probably due to its weak thermal stability was not detected. In analogy the two ethyldibenzofurans were also absent in these samples. Benzo[*b*]naphthofurans were not abundant in the mature *Mesocalamites cf. Taitianus* (Table 7.11). While the *Sigillaria* and the East Greenland sample of lowest maturity lack the presence of alkylxanthones and -carbazoles, the *Mesocalamites cf. Taitianus* and the Russian coal are characterised by the absence of alkylxanthones, only (Table 7.11).

The presence of alkyldibenzothiophenes in all of the samples can be attributed to the fact that these compounds are preferentially formed at elevated maturities. In accordance with the previously discussed compound classes, the composition of alkyldibenzothiophenes of the *Mesocalamites cf. Taitianus* significantly influences the correlation of the more mature type II-III samples. Due to its enhanced maturity, but in contrast to its lean content on total sulphur, the sample is characterised by significantly enhanced proportions of alkyldibenzothiophenes. In agreement with the elevated amounts of alkylphenanthrenes of the sample, alkyldibenzothiophenes show a strong correlation to 2- and 3-methylphenanthrene and 2,6- and 2,7-dimethylphenanthrene, which are the most stable isomers of this compound class. Including the *Mesocalamites cf. Taitianus* alkyldibenzothiophenes, except for 1-methyl- and 1-ethyldibenzothiophene also strongly correlate to alkylfluorenes and some of the $C_{(0-1)}$-2-phenylnaphthalenes. However, these good correlations with the findings for the North English coals, result from the strong influence of the *Mesocalamites cf. Taitianus*. When excluded, correlations of alkyldibenzothiophenes to other compounds classes are weak. These findings are in agreement with the behaviour for the other compound classes of this sample group. The low correlations result from the fact, that the different origins and composition of the organic matter for the more mature type II-III samples are recognisable.

The absence of alkylcarbazoles for the mature type II-III samples is accompanied by the lack of alkylxanthones. It has been stated previously for the immature

Table 7.11: Occurrence of alkyldibenzothiophenes (DBT), -carbazoles (C), -dibenzofurans (DBF), benzo[*b*]naphthofurans (BNF) and -xanthones (X) in mature type II-III organic matter

Sample	DBT	C	DBF	BNF	X
E 49748	+	+	++	++	+
E 49749	+	+	++	++	+
E 49750	+	+	++	++	+
E 49751	+	-	++	++	-
E 48990	+	+	++	++	-
E 48425	+	+	++	-	-
E 48430	+	-	++	++	-

++:present, +:present to low amounts, -:absent

samples that this does not indicate an unambiguous relationship concerning the origin of the two compound classes. It may also indicate a similar thermal stability of the alkylcarbazoles and -xanthones. In contrast to the North English samples, but in analogy to the less mature coals, distribution of methylcarbazoles varies more significantly. Actually the predominance of 1-methylcarbazole, the most abundant isomer for North English coals, is relatively depleted for the more mature samples. Whether this can be attributed to thermal stability however is insecure. Shielded alkylcarbazoles i.e. with methyl groups adjacent to the nitrogen in common are known to be predominant (Frolov *et al.*, 1989). Due to the relative enhanced maturity of the samples the recognition of a specific contribution is improbable. However the set of mature sediments often was characterised by strong variations not correlating to their elevated maturity level. In accordance with the suggestions for 1-methyldibenzofuran an enhanced releasement of bonded natural compounds at elevated maturities is suggestible. However, variations of different isomers for alkylcarbazoles though stronger than for the North English coals still are relatively weak. This supports the hypothesis based on the observations for all previously discussed samples, that they do not originate from a specific source.

Correlation of individual alkyldibenzofurans, in accordance to the general behaviour of this subset of samples, is weak. According alkyldibenzofurans T_{max} again seems to be a better indicator of thermal maturity than vitrinite reflectance for the more mature type II-III samples. Again, due to its strongly different

composition, values for the *Mesocalamites cf. Taitianus* have been excluded. Nevertheless a relative increase of 1-methyldibenzofuran with neither an increase of vitrinite reflectance and of T_{max} is observed. Contrary to previously discussed subsets of samples, correlation of individual isomers for alkyldibenzofurans is enhanced. This may account for an enhanced progression of isomerisation reactions. Methyldibenzofurans in general show a strong correlation to the first eluting C_1-2-phenylnaphthalene. This was already observed for alkyldibenzofurans of the immature type II-III coals.

A strong correlation is also observed for the first eluting C_1-2-phenylnaphthalene and benzo[*b*]naphthofurans. A biogenic relationship has already been suggested based on the observations for the North English coals. A correlation because of the enhanced thermal stability is improbable, due to benzo[*b*]naphthofurans being absent in the mature fossil. In contrast, correlations for the last eluting benzo[*b*]naphthofuran to the other isomers are weak. Actually this may account for a depleted thermal stability of this compound. Nevertheless it does not contradict the hypothesis that all four compounds originate from a similar biogenic source.

For the more mature samples, xanthone and methylxanthones were only detected in three samples from East Greenland. These samples contrary to previously discussed ones are not characterised by elevated proportions of pristane. Additionally the presence of alkylxanthones in these samples expands the maturity range of the North English coals.

7.4.4 Group IV

In contrast to all previously discussed samples, the type I samples are rare in heterocyclic compounds. The biodegraded sample from South France lacks the presence of all compound classes (Table 7.12). Alkyldibenzofurans and benzo[*b*]naphthofurans (Table 7.12), except for the two ethyldibenzofurans were generally abundant. The two ethyldibenzofurans were present in the two non biodegraded samples from South France, only. Alkyldibenzothiophenes in contrast were generally not detected in the samples from South France (Table 7.12), while the Spitsbergen coal lacks 4-ethyldibenzothiophene and 4,6-dimethyldibenzothiophene. The absence of alkyldibenzothiophenes in the samples from South France probably can not be attributed to their weakness in organic matter, due to the fact that they are the only type I samples where ethyldibenzofurans were present in quantifiable amounts. However, contents of total sulphur are low for these samples. Alkylxanthones were generally not detected, while alkylcarbazoles were only present in the Spitsbergian coal (Table 7.12).

The distribution of alkyldibenzothiophenes in analogy to the distribution of aromatic hydrocarbons in these samples, shows no correlation to maturity. However, in correspondence to the North English coals and the more mature type III samples, alkyldibenzothiophenes show a good correlation to 2- and 3-methylphenanthrene and 2,6- and 2,7-dimethylphenanthrene. This indicates, that although distribution of different compound classes for the type I samples is not significantly influenced by the maturity of the samples, the factors influencing the amounts of thermodynamically more stable isomers are related (van Aarssen *et al.*, 2001). Besides this, alkyldibenzothiophenes show good correlation to alkylfluorenes, -fluoren-9-ones, many alkylbiphenyls but only to 2-phenylnaphthalene and the third eluting C_1-2-phenylnaphthalene. The hypothesis based on the observations for the North English coals, that alkyldibenzothiophenes, -fluorenes and -fluoren-9-ones correlate due to their thermal stabilities therefore is supported.

The type I samples except for the Devonian one, lack the presence of alkylcarbazoles. The sample is characterised by enhanced proportions of pristane indicating an oxic environment at least at early stages of deposition. The findings

Table 7.12: Occurrence of alkyldibenzothiophenes (DBT), -carbazoles (C), -dibenzofurans (DBF), benzo[*b*]naphthofurans (BNF) and -xanthones (X) in immature type I organic matter

Sample	DBT	C	DBF	BNF	X
E 48478	-	-	++	++	-
E 48479	-	-	++	++	-
E 48480	-	-	-	-	-
E 48985	+	-	++	++	-
E 48986	+	-	++	++	-
E 48987	+	-	++	++	-
E 48992	+	+	++	++	-

++:present, +:present to low amounts, -:absent

again contradict the hypothesis that alkylcarbazoles are formed in the presence of reduced nitrogen at early stages of diagenesis. Actually the absence of alkylcarbazoles in most of the type I samples may indicate that the compounds are specific contributors to type II-III kerogen. However the detection of these compounds in organic matter originating from marine sources (Li *et al.*, 1995, 1997; Horsfield *et al.*, 1998; Clegg *et al.*, 1997; Bakr and Wilkes, 2002) contradicts this hypothesis. Another likely explanation is that alkylcarbazoles are formed at elevated maturity ranges. This indeed correlates to the fact, that in comparison to the majority of the type I samples, the maturity of the Devonian sample is relatively enhanced. In the most immature type II-III samples alkylcarbazoles were also absent and Clegg *et al.* (1998b) additionally found a dependence of relative amounts of alkylcarbazoles on the thermal maturity of the sediments. The distribution of methylcarbazoles for this sample corresponds to the distribution of these compounds in the low and high maturity type II-III samples. In agreement with the observations for the low maturity type II-III coals, this indeed might indicate that the distribution of alkylcarbazoles in the North English coals is controlled thermally while this is not true for the rest of the sample sets. This for immature samples generally points to a strong contribution of specific isomers which are not necessarily the most stable ones. For the mature samples this should be ruled out, while the set investigated in this thesis often was characterised by composition of compounds not strongly corresponding to thermal maturity.

The relative amounts of individual alkyldibenzofurans for the type I samples according to vitrinite reflectance are characterised by a relative decrease. This was observed for many aromatic hydrocarbons in this subset. The absence of ethyldibenzofurans in many of the samples is in analogy to the type II-III coals of low maturity. This strongly supports the suggestion that the formation of ethyldibenzofurans is controlled kinetically. This may indicate, that the compounds have specific precursors and are released at certain temperatures only, while they are destroyed at higher levels of thermal maturity. For type I samples individual alkyldibenzofurans show strong correlation. This is contrary to observations made for the former discussed subsets of samples. It supports the hypothesis, that these compounds, at least for organic matter not predominantly originating from terrestrial sources are not characterised by strong contribution of specific isomers. Actually it has been mentioned previously, that alkyldibenzofurans are supposed to originate from terrestrial sources.

For type I samples, in contrast to all previously discussed samples, correlation for benzo[*b*]naphthofurans and the forth compound is weak. While benzo[*b*]naphtho[*1,2-d*]furan correlates to all isomers, this is slightly the case for benzo[*b*]naphtho[*2,3-d*]furan and the forth compound. A very strong correlation between benzo[*b*]naphtho[*1,2-d*]furan and benzo[*b*]naphtho[*2,3-d*]furan indicates a common source of the two compounds. They, additionally are characterised by a strong correlation to retene and 1-methylphenanthrene, supporting the hypothesis that they are terrigenous markers.

The general absence of alkylxanthones in the type I samples may indicate, that these compounds originate from terrestrial sources. This indeed is supported by the fact, that at least the sample from Spitsbergen is characterised by a vitrinite reflectance where alkylxanthones normally were abundant in other samples. However, the general presence of alkylxanthones within a certain maturity range was not observed previously. Therefore the absence in the type I samples may indeed have occurred accidental.

7.5 Resumée

The subdivision of the investigated samples into four subsets proofed to be convenient. While the set of North English coals (Group I) correlates to organic matter, where catagenetical processes proceed but contribution from specific sources are still recognisable, the composition for the more immature subset (Group II) strongly points to contribution from specific sources. The more mature samples (Group III) however, do not correspond to an enhanced catagenesis of type II-III kerogen organic matter, only. Effects of deposition, origin of organic matter but probably also mineral matrix effects are recognisable. The subset of type I kerogen samples (Group IV) helps to assess which observations indeed are typical for terrigenous organic matter, and which are a general characteristic of organic matter, that has not been subject to strong catagenetical processes. Type I kerogen organic matter for many parameters indeed shows significant deviations from the type II-III kerogen samples. With two exceptions, biodegradation is supposed to play a minor role according the composition of extractable organic matter for the investigated samples.

For the three subsets of samples containing predominantly terrigenous organic matter exceptions have to be considered. The North English coals except for the samples from Throckley form a relative homogenous subset. The depleted values for many maturity parameters for the Throckley samples are presumed not to originate from sorptive protection mechanisms. A weak mobile phase not corresponding to the thermal maturity was assumed and that maturation effects only affected macromolecular organic matter, while low molecular weight organic matter to some extent preserved a more biogenic composition. A sorptive protection mechanism in contrast has been attributed to influence the composition of mature samples from East Greenland. In general the samples of the most mature subset are characterised by strong variabilities in composition, indicating, that environmental factors are still recognisable at elevated vitrinite reflectances.

The composition of alkylnaphthalenes and -phenanthrenes and their corresponding functionalised analogues is strongly interrelated for all investigated samples. Especially the oxidation of ethylnaphthalenes to the analogue naphthylketones

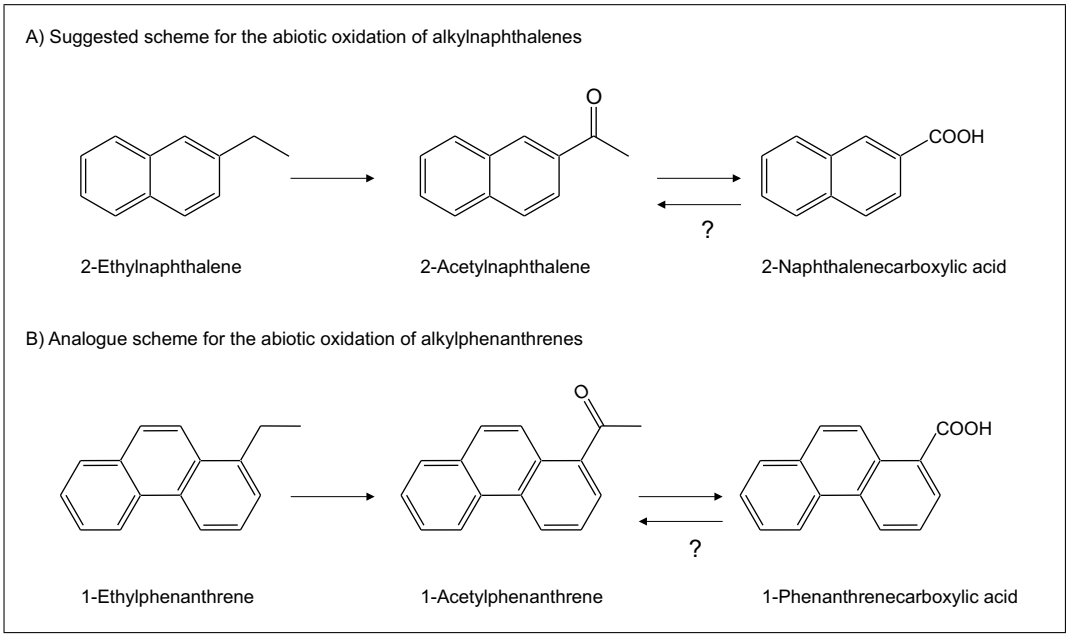

Figure 7.37: Suggested scheme for the oxidation of A) alkylnaphthalenes and B) alkylphenanthrenes occurring in sedimentary organic matter, while the oxidation to ketones and aldehydes is supposed to occur easily the formation of carboxylic acids is suggested to require elevated temperatures and probably also oxic conditions

occurs easily in sediments and does require neither elevated thermal stress nor strongly oxic conditions (Fig 7.37). Additionally the corresponding ketones and aldehydes are of enhanced thermal stability, due to their presence over the entire maturity range investigated in this thesis. It is suggested that 2-ethylnaphthalene is oxidated in favour due to the ratio of 2-naphthylketone/1-naphthylketone in comparison to the ratio of 2-ethylnaphthalene/1-ethylnaphthalene normally being elevated. This in the context of this thesis was explained by a sterical hinderance for the oxidation of 1-substituted naphthalenes. Oxidation of aldehydes and ketones to the corresponding carboxylic acids in contrast is supposed to depend on thermal maturation (Fig. 7.37). Alkylnaphthalene- and alkylphenanthrenecarboxylic acids with one exception are only present in samples of elevated maturity. This clearly shows, that the compounds are not formed artificial during sample preparation but prior in the sedimentary record. Their absence in the most mature samples points to a destruction. It is suggested in this thesis that carboxylic acids based on the naphthalene and phenanthrene skeleton are formed within an elevated maturity range, while they due to defunctionalisation processes again are

destroyed at higher maturity levels. The abiotic formation of carboxylic acids requires the presence of oxidants. These may be inorganic compounds that have been subject to oxidation at early stages of sedimentation and which in turn serve as oxidants at later stages. Besides these abiotic formations, the compounds and especially alkylnaphthalenedicarboxylic acids may also be formed as intermediates during biodegradation.

Based on the observations for the four subsets, the original amounts of alkylnaphthalenes in relation to alkylphenanthrenes were suggested to be represented by the relative proportions of the corresponding acids more exactly. Figures 7.15, 7.20, 7.24, 7.25 show, that $C_{(0-1)}$-naphthalenes are subject to enhanced volatilisation and that this strongly influences the relative amounts of this compound class. However, except for few of the more mature samples showing an enhanced proportion of alkylphenanthrenes and -phenanthrenecarboxylic acids, respectively, a relative increase of tricyclic aromatic hydrocarbons with increasing maturity is neither observed for aromatic hydrocarbons nor for the corresponding carboxylic acids.

It should be recognised that the depletion of $C_{(0-1)}$-naphthalenes due to volatilisation for some samples does not influence the significance of biogenic information that would be gained by an unchanged composition. Nevertheless especially for the maturity levels of the North English coals, individual alkylphenanthrenes are characterised by an enhanced contribution from specific sources, while distributions of alkylnaphthalenes are supposed to be less specific. This is well-founded by the fact, that the former compounds are characterised by weak correlations in comparison to alkylnaphthalenes. However, at higher maturity ranges composition of alkylphenanthrenes also becomes more homogenous, supporting this hypothesis. It is presumed that alkylnaphthalenes are formed or released at lower thermal maturities and that isomerisation of these compounds occurs prior to the one of alkylphenanthrenes. This is strongly supported by the fact that C_{3-4}-naphthalenes show an increase of relative amounts with increasing maturity for low maturity samples, while they show a decrease with increasing maturity for the North English coals. This in contrast is not observed for alkylphenanthrenes. Besides this biogenic relationships of alkylnaphthalenes and -phenanthrenes are rather complex

Table 7.13: Compound classes formed randomly in sediments listed in order of formation based on their presence in the samples in general and the variability in amounts of isomers (It should be noticed that alkylfluoren-9-ones are suggested to originate from alkylfluorenes and that for alkylxanthones neither a random formation nor a formation from specific precursors was indicated)

Compound Class	variability in isomers
C_{0-2}-biphenyls	weak
C_{0-2}-fluorenes	weak
C_{0-1}-fluoren-9-ones	weak
C_{0-2}-carbazoles	weak
C_{0-1}-dibenzothiophenes	strong

Table 7.14: Compound classes where a specific terrestrial precursor is suggested

Compound Class	suggested precursor	reaction
C_{0-1}-phenyl-2-naphthalenes	lignans	defunctionalisation
C_{0-2}-dibenzofurans	lichens	defunctionalisation
Benzo[*b*]naphthofurans	terrigenous	condensation

and will partly be discussed in the following chapter dealing with the chemotaxonomic significance of individual compounds. In general it is assumed that retene is released during the entire maturity range investigated in this study. The compound is easily transformed into 7-ethyl-1-methylphenanthrene, while correlation to 1,7-dimethylphenanthrene is weak probably due to the different origins of 1,7-dimethylphenanthrene. Besides retene agathic acid is another potential source of 1,7-dimethylphenanthrene. This is indicated by the strong correlation of this compound to 1,2,5-trimethylnaphthalene for the immature type II-III kerogen samples. Additionally a biogenic relationship between 1,2,7-trimethylnaphthalene and cadalene is indicated while the specific precursor of 1,2,7-trimethylnaphthalene is unknown.

In analogy to the observations made for alkylnaphthalenes and their corresponding ketones, methylfluorenes and -fluoren-9-ones normally are characterised by a strong interdependence in relative amounts. However, while 2-ethylnaphthalene appeared to be more susceptible to oxidation than 1-ethylnaphthalene, different isomers of methylfluorenes show no preference for oxidation. Relative amounts

of fluorene and fluoren-9-one in contrast do not correlate, indicating that the compounds i.e. especially some amounts of fluoren-9-one are formed via another pathway than the methylated analogues. Cyclisation of biphenylcarboxylic acids is supposed to play a minor role in the formation of alkylfluoren-9-ones.

In contrast to alkylfluorenes being minor contributors to the fraction of aromatic hydrocarbons, alkylfluoren-9-ones normally are highly abundant in the low-polarity NSO compound fraction. This, in agreement with the hypothesis made for ethylnaphthalenes and naphthylketones shows, that oxidation of the aromatic compounds occurs easily in sediments. The redox potential of the sediments but also the thermal stress are negligible factors according the oxidation of the activated, benzylic position of the fluorene skeleton. If a specific source would have account for the amounts of individual isomers, isomerisation reactions were supposed to occur at low thermal maturities. The composition of methylfluorenes and -fluoren-9-ones respectively is almost identical for the investigated samples except for one. The absence of alkylfluoren-9-ones in the Devonian sample on the other hand is striking. However it is not supposed to indicate an age specific characteristic.

For alkylbiphenyls neither a strong correlation to alkylfluorenes nor to alkylphenylnaphthalenes is observed. The absence of alkylbiphenyls in some immature samples, where alkylfluorenes were present, strongly indicates that alkylbiphenyls are not the only potential precursors of alkylfluorenes. The weak correlation between alkylbiphenyls and -phenylnaphthalenes refers to the fact that the compounds are not formed via an equal pathway, i.e. a radical induced phenylation. While the composition of alkylbiphenyls is of little significance, their predominant formation from lignin derived precursors is ruled out due to their absence in the two German coals. For these two samples contribution of terrestrial derived organic matter normally is strongly recognisable. Alkylbiphenyls probably are formed randomly and are not characterised by elevated thermal stabilities. They were present in low amounts in the subset of mature sediments.

For alkylphenylnaphthalenes a natural precursor is proposed. Many constituents of lignans base on the 1-phenylnaphthalene skeleton. Although only $C_{(0-1)}$-2-phenylnaphthalenes were investigated, these compounds, in analogy to alkylflu-

orenes show a relative increase with increasing maturity. It is presumed that isomerisation results in the formation of alkyl-2-phenylnaphthalenes accompanied by the depletion of the corresponding alkyl-1-phenylnaphthalenes. The isomerisation is presumed to depend on the maturity of organic matter and probably occurs during almost the entire maturity range investigated in this study. Although correlation between $C_{(0-1)}$-2-phenylnaphthalenes and -fluorenes have normally been strong, this does not account for the type I samples, indicating, that $C_{(0-1)}$-2-phenylnaphthalenes indeed may have a terrigenous contributor.

While for all other compound classes a suggestion existed whether they have recognisable biogenic precursors or are formed randomly in sediments, this does not account for the compounds incorporating a hetero cycle. For alkyldibenzothiophenes the findings in this study support the hypothesis that they have no specific source but are formed randomly in sediments (Arpino *et al.*, 1987; Sinninghe Damsté and de Leeuw, 1990). However the redox potential of sediments based on the ratio of pristane/phytane shows that reducing conditions at early stages of deposition are not the only factor influencing the relative amounts of this compound class. The relative amounts of total sulphur show an influence. These amounts accord to the amounts of reduced sulphur that may be available under optimal conditions. The predominant factor however seems to be the magnitude of maturity. A strong correlation of alkyldibenzothiophenes to alkylfluorenes and -2-phenylnaphthalenes, observed for the North English coals and the more mature samples supports the hypothesis that thermal maturity is the most important factor. For samples of low maturity correlation between alkylfluorenes and -dibenzothiophenes are weak. This indicates that alkyldibenzothiophenes are formed later than alkylfluorenes in sediments. Their formation requires thermal maturity while their precursors are formed randomly earlier. Contrary to alkylfluorenes isomerisation reactions are of enhanced importance for alkyldibenzothiophenes within the maturity range investigated in this thesis. This fact indicates that the formation of alkyldibenzothiophenes by coincidence produces certain isomers in preference. Actually this accords to the hypothesis of Sinninghe Damsté and de Leeuw (1990) (Fig. 6.21).

In correlation to alkyldibenzothiophenes, alkylcarbazoles also show no indication for a contribution from a specific source. In this thesis it therefore was suggested

that they are also formed randomly in sediments. In analogy to alkyldibenzothiophenes a strong correlation between reducing conditions at early stages of sedimentation and relative amounts of alkylcarbazoles is not observed. In contrast many of the low maturity samples where alkyldibenzothiophenes were abundant lack the presence of alkylcarbazoles. Additionally the composition of individual isomers does not vary significantly for most of the samples, indicating that isomerisation reactions are of depleted importance. The last mentioned findings indicate that either alkylcarbazoles are formed earlier than alkyldibenzothiophenes or that they are formed via another pathway not resulting in the formation of specific isomers. The absence of alkylcarbazoles in many of the immature samples actually indicates that a different formation pathway is more likely. It is improbable that isomerisation reactions occur significantly more easily for alkylcarbazoles than for alkyldibenzothiophenes.

Alkyldibenzofurans and benzo[*b*]naphthofurans correspond to organic matter originating from terrestrial sources. This in contrast to the findings for alkyldibenzothiophenes and -carbazoles indicates that the two compound classes are not formed randomly in sediments. In correspondence to alkylphenanthrenes especially alkyldibenzofurans often are characterised by weak correlations. Contribution from a specific source is especially assumed for 1-methyldibenzofuran. The compound often is characterised by weakest correlation to other methyldibenzofurans and may, according to the suggestions of Radke *et al.* (2000) originate from constituents of lichens. The absence of ethyldibenzofurans for both, samples of low maturities and elevated maturities indicates that their formation is controlled kinetically. Otherwise due to their depleted thermal stability, they were supposed to be present in low maturity samples. Their absence in samples of elevated maturity corresponds to their low thermal stability.

Benzo[*b*]naphthofurans show strong correlation among all three isomers and the forth compound. They however are present in all samples with no respect to maturity. This strongly indicates, that they are formed easily in sediments and do not require enhanced thermal stress. Condensation of an ubiquitous precursor may result in their formation. Benzo[*b*]naphtho[*2,3-d*]furan shows a slight depletion of relative amounts in comparison to the two other isomers at elevated maturity levels.

This does indicate that the compound is the least stable isomer. Correlation of the four compounds are more pronounced for terrestrial organic matter indicating a specific contribution.

Speculations on the origin of alkylxanthones due to their absence in many of the investigated samples are vague. Their presence might be restricted to samples of elevated maturities that have been deposited under oxic conditions. However the presence of these compounds in some of the samples from East Greenland contradicts this hypothesis. Their absence in type I kerogen samples may indicate that they originate from terrigenous precursors but may also be due to low thermal maturities.

7.6 Chemotaxonomic Significance of Compound Classes and Individual Compounds

7.6.1 Compounds and Compound Classes of Little Chemotaxonomic Value

Organic residues often are of low selectivity i.e. they are present in many living organisms and their abundance in fossil organic matter does not indicate the presence of a specific organism. Compounds like *n*-fatty acids, sterols and regarding plants chlorophyll, are widely distributed in living organisms, and therefore are of little value for determining an unambiguous chemotaxonomic relationship for these compounds. Another characteristic of organic residues is, that their significance often is limited as the specific molecular composition is lost due to alteration processes because of biodegradation or isomerisation due to low thermodynamic stabilities. Some compounds preserve their original constitution at enhanced thermal maturation and are resistant against biodegradation while others are broken down into constituent parts and therefore retain little or no chemotaxonomic significance.

Changes in the composition of extractable organic matter, that can be directly related to evolutionary trends are rare. A significant change in the composition of extractable organic matter probably is the presence of long-chain *n*-fatty acids and -alkanes, attributed to higher plants. The absence of these compounds is related to the Ordovician or to organic matter that does not predominantly originate from terrestrial sources. The samples investigated in this study are younger than the Ordovician and contain organic matter that predominantly is derived from terrestrial sources. However long-chain *n*-fatty acids and -alkanes are rare in the majority of the investigated samples. For *n*-alkanes these findings correlate to the enhanced maturity for most of the samples, resulting in an unimodal distribution. For *n*-fatty acids however, the CPI_{SFA} in comparison to the CPI_{LFA} (Table 6.9) strongly indicates, that long-chain *n*-fatty acids have not been significant contributors to the organic matter of the samples. Actually the rapid

irregular decrease towards higher molecular weights correlates to the findings of Disnar and Harouna (1994) for *n*-alkanes. The authors suggested that the absence of long-chain *n*-alkanes is a characteristic of non-flowering strata. Due to their genetic relationship this should also account for long-chain *n*-fatty acids. However, the strong predominance of these compounds in few of the immature type II-III samples shows, that even non-flowering plants possess the ability to produce long chain *n*-fatty acids. Their strong predominance in the two German coals and one sample from the Moscow Basin indicates, that a contribution of a specific Carboniferous flora may account for this. A possible explanation might be that the majority of the locations where the samples are from were swamps. In swamps humic conditions probably have been present. These environmental conditions may have limited the necessity to produce protective coatings for many plants. This however would indicate, that the characteristic of producing these kinds of protective coatings due to protection from evaporation have not been a solely important characteristic for the inhabitance of terrestrial environments by plants.

Although alkylphenanthrenes and -dibenzofurans have been assigned to be terrestrial markers, their significance is limited by the fact that they are the result of defunctionalisation processes, molecular breakdown and aromatisation. Budzinski *et al.* (1995) attributed a terrestrial but also marine character to many individual alkylphenanthrenes. However, specific and therefore unambiguous precursors are seldomly known. 1-Methylphenanthrene as a terrestrial marker for example is supposed to originate from retene and pimanthrene, which do not necessarily originate from the same biological precursor (Ellis *et al.*, 1996). 1,2,8-Trimethylphenanthrene has recently been discussed as a biomarker. The compound has been highly abundant in samples of the Lower Cretaceous and younger (Budzinski *et al.*, 1995). The authors suggested that it may derive from the degradation of triterpenoids or hopanoids that show an ubiquitous presence. Additionally high proportions of 1,2,8-trimethylphenanthrene according to Budzinski *et al.* (1995) indicate a low maturity of organic matter. Kruge (2000) investigated samples extending the Devonian to Upper Carboniferous period. The author focussed on the distribution of polycyclic aromatic hydrocarbons and did not investigate the distribution of alkylphenanthrenes in particular. Although he could not assign individual trimethylphenanthrenes unambiguously, he according to retention

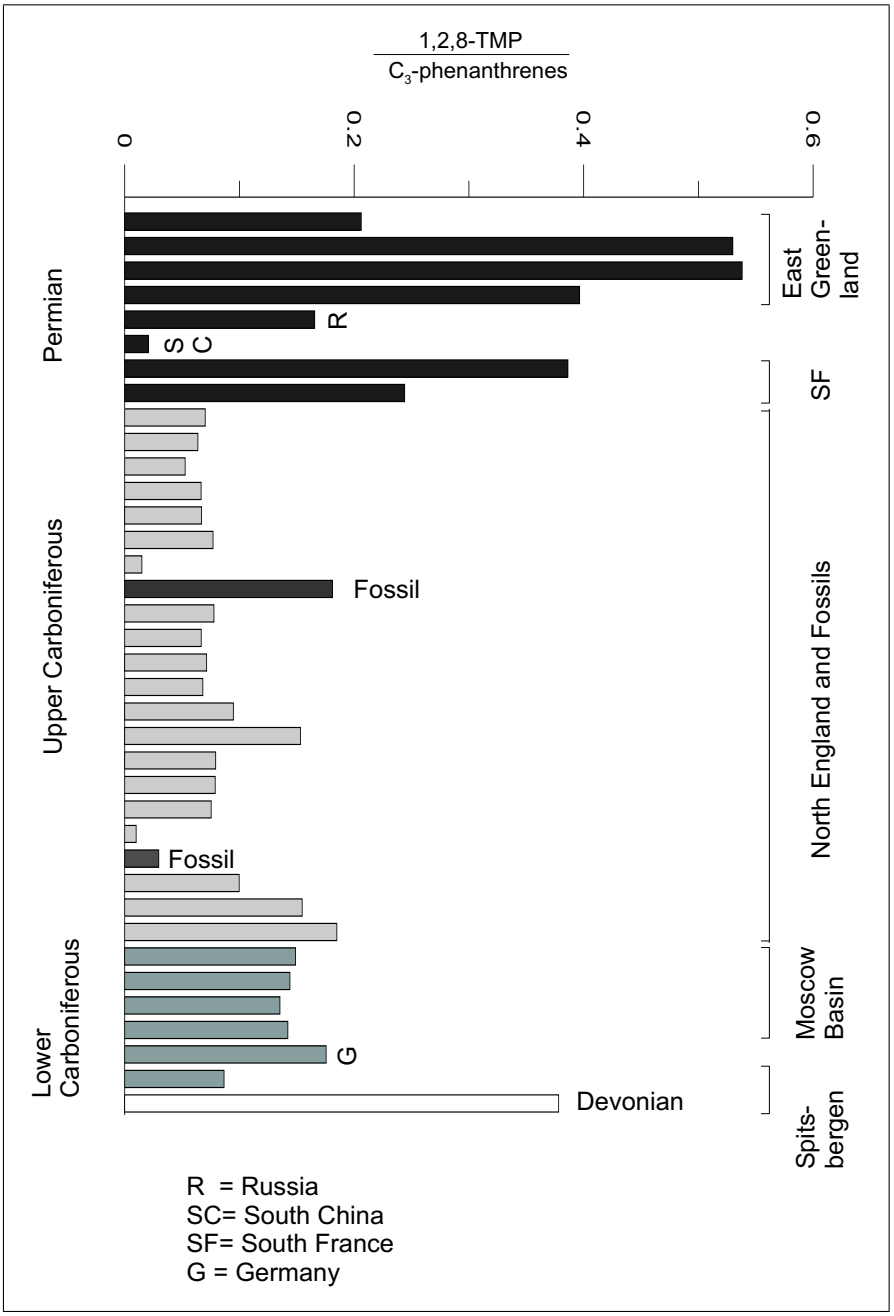

Figure 7.38: Bar diagram showing the relative amounts of 1,2,8-trimethylphenanthrene (1,2,8-TMP) to the sum of C_3-phenanthrenes, except the ones that have often been rarely abundant

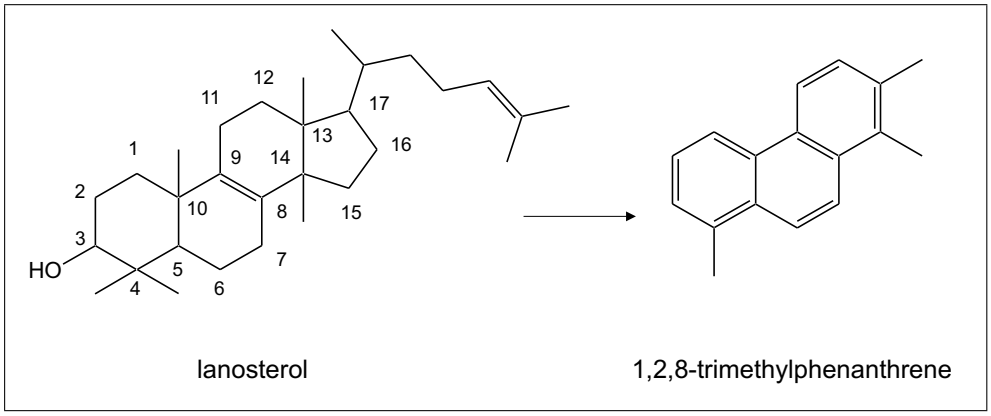

Figure 7.39: Formation of 1,2,8-trimethylphenanthrene via dehydrogenation of lanosterol after King and de Mayo (1964)

indices, suggested the last eluting one to be 1,2,8-trimethylphenanthrene. Relying on the three chromatograms given by the author, the relative amounts of 1,2,8-trimethylphenanthrene besides the maturity of the samples may also depend on the type of organic matter.

In the present study, 1,2,8-trimethylphenanthrene has been identified by coelution with an authentic standard. Its concentration, in comparison to the amounts of summed C_3-phenanthrenes, shows a significant increase for the majority of the Permian samples (Fig. 7.38). In correspondence to the studies of Budzinski *et al.* (1995) a dependence of relative amounts on the thermal maturity can not be excluded. Samples characterised by enhanced maturities are characterised by a relative depletion of 1,2,8-trimethylphenanthrene in comparison to other isomers. Although, regarding T_{max}, the vitrinite reflectances and therefore the maturity of the samples from East Greenland may be overestimated, the relative amounts of 1,2,8-trimethylphenanthrene are significantly enhanced. Additionally the compound is also relatively enriched in most of the low maturity samples of the Lower Carboniferous. Besides the possible dependence on thermal maturity, the high proportions of 1,2,8-trimethylphenanthrene for most of the Permian samples may indicate an age specific trend. Respecting the low maturities of the Lower Carboniferous samples the high proportions of 1,2,8-trimethylphenanthrene for the Permian samples are significant. However the high amounts that have been proposed for Devonian samples within the studies of Kruge (2000) correlate to the

high proportions of 1,2,8-trimethylphenanthrene for the Devonian sample of the present study. This indicates that the potential organism that produces the precursors of 1,2,8-trimethylphenanthrene may have existed in the Devonian while it was less dominant in the Carboniferous. It is also possible that for both the Devonian and the Permian different organisms are responsible for the high proportions of 1,2,8-trimethylphenanthrene.

Due to the fact, that the relative amounts of 1,2,8-trimethylphenanthrene do not exclusively depend on maturity and can not be attributed to an age specific behaviour unambiguously, environmental factors may also account for the proportions of 1,2,8-trimethylphenanthrene. Amounts of 1,2,8-trimethylphenanthrene are more enhanced for the two samples from East Greenland that showed higher amounts in liptinites. Besides their low thermal maturity most of the Lower Carboniferous samples are also characterised by enhanced proportions of liptinites. The two samples from South France are supposed to contain high amounts of marine derived material. It therefore is presumable, that 1,2,8-trimethylphenanthrene does not originate from a terrestrial source. Steranes and their biological precursor are potential precursors of 1,2,8-trimethylphenanthrene (Fig. 7.39). The dehydrogenation of lanosterol led to the formation of 1,2,8-trimethylphenanthrene (King and de Mayo, 1964). The two methyl groups at position 13 and 14 of the steroid skeleton are transformed into the methyl groups of 1,2,8-trimethylphenanthrenes (Fig. 7.39). It therefore is presumable, that steroids sharing a methyl group at position 4-, 13-, 14- of the steroid skeleton do also form 1,2,8-trimethylphenanthrene. However steroids originate from the enzymatic oxidation and cyclisation of squalene and are ubiquitous. While lanosterol is a precursor of animal steroids, cycloartenol, which might also yield in the formation of 1,2,8-trimethylphenanthrene is a precursor of plant steroids (Killops and Killops, 1993). Both compounds are intermediates within the biosynthesis of steroids and are supposed to be of depleted thermal stability. The occurrence of compounds showing a lanostane skeleton has rarely been recorded. The samples where compounds of the lanostane type have been present were characterised by either high contents of sulphur (Peng *et al.*, 1998) or low pristane/phytane ratios accompanied by high proportions of gammacerane (Chen and Summons, 2001). These characteristics are typical for marine or hypersaline environments. In gen-

eral steranes, the likely degradation products of naturally occurring sterols are supposed to be highly abundant in organic matter predominantly deriving from marine sources (Peters and Moldowan, 1993). Therefore the findings of high proportions of 1,2,8-trimethylphenanthrene in liptinite-rich samples indeed indicate an enhanced contribution of marine derived organic matter being responsible for elevated amounts of the compound. However it can not be excluded, that respecting the suggestions of Budzinski *et al.* (1995) other compounds may also be important precursors of 1,2,8-trimethylphenanthrene. Indeed the samples showing elevated amounts of 1,2,8-trimethylphenanthrene are not always characterised by high proportions of sulphur or low ratios of pristane/phytane. Additionally the high amounts of 1,2,8-trimethylphenanthrene for the *Sigillaria* (Fig. 7.38) are significant. The sample is characterised by the absence of marine derived organic matter and shows a relatively elevated thermal maturity. Therefore tetracyclic triterpenoids for example of the dammarane type may also be potential precursors of 1,2,8-trimethylphenanthrene (Masuda *et al.*, 1983).

The unambiguous origin of alkyldibenzofurans, although they may derive from terrestrial sources, is also insecure. However, it has been suggested that some of these compounds may be derived from constituents of lichens. Whether this is the only possible source, yet however is unknown. This is due to the fact that systematic investigations on alkyldibenzofurans have become of interest in recent years only. The distribution of 1-methyldibenzofuran for samples of this study actually supports the hypothesis, that the compound might originate from constituents of lichens. Due to the fact, that constituents of lichens possessing a dibenzofuran skeleton often also are 1,9-alkylsubstituted the structure assignment of C_2-dibenzofurans would be of high value. Due to the oxic depositional environments for many samples, however, the loss of functionalised groups adjacent to the aromatic skeleton of alkyldibenzofurans may not proceed easily. Therefore it might be important to prove defunctionalisation in laboratory experiments. It might be also presumable that the loss of these groups occurs at elevated thermal maturation, and that functionalised alkyldibenzofurans are present in the high-polarity NSO compound fraction that has not been investigated. Respecting that defunctionalisation normally is due to increasing thermal stress this might be of specific relevance for samples of low maturities.

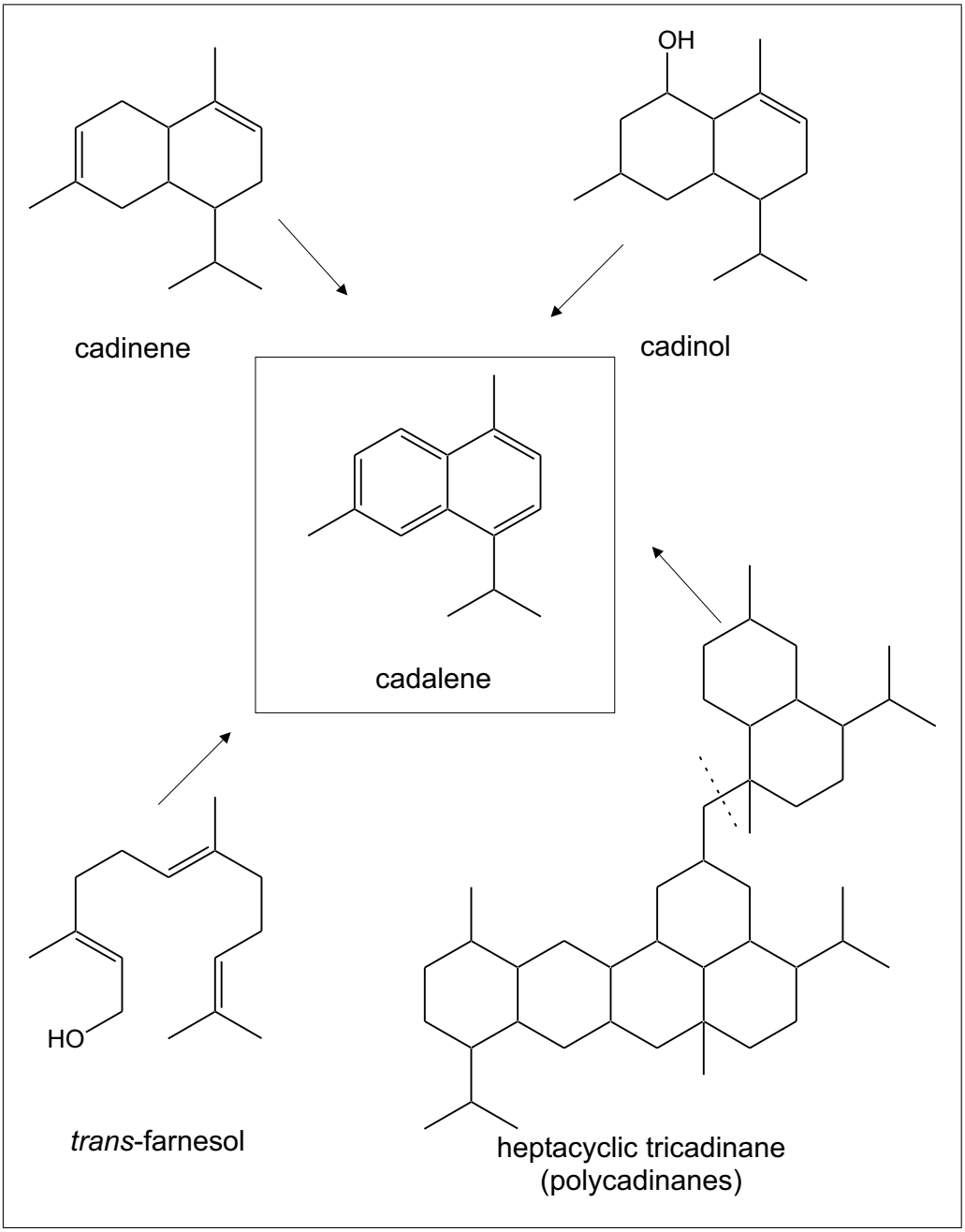

Figure 7.40: Biological precursors of cadalene after Douglas and Mair (1965); Simoneit (1986); van Aarssen *et al.* (1992)

This may also account for lignan derived alkylphenylnaphthalenes. The functionalised analogues of these compounds might be present in the high-polarity NSO compound fraction of the low maturity samples, and loss of the groups may account for the enhanced presence of alkylphenylnaphthalenes at elevated maturities. However, the isomerisation then is supposed to proceed quickly, due to 2-phenylnaphthalenes often being predominant. Lignans as possible precursors of alkylphenylnaphthalenes in analogy to *n*-fatty acids are of little chemotaxonomic significance. Lignans are constituents of many higher plants but also of liverworts. Therefore their presence is of little chemotaxonomic value. This to some extend does also account for the potential relationship between high amounts of 1-methyldibenzofuran and the presence of lichens. Although the presence of lichens can be dated back to the Early Devonian (Taylor *et al.*, 1995), they have not been an important subject to investigations with respect to the evolution of higher plants. They probably due to their symbiosis of fungi and algae evolved separately.

Another unspecific biomarker is cadalene. It commonly is accepted as a marker for higher plants (Simoneit, 1986; Peters and Moldowan, 1993). However, its precursors are ubiquitous in resins and essential oils of these plants. Aromatisation of cadinenes and cadinols, the cyclisation and aromatisation of farnesol, but also the breakdown and aromatisation of polycadinenes is supposed to result in the formation of cadalene (Fig. 7.40). The presence of this sesquiterpene in most of the samples extending the Lower Carboniferous to Upper Permian period therefore is of little chemotaxonomic value.

The chemotaxonomic significance of vanillin due to its presence in bryophytes (Thomas, 1986) may be of little value, as it is no exclusive oxidation product of lignin or lignin-like constituents. The finding of vanillin in organic matter from the Silurian by Niklas and Pratt (1980) therefore does not unambiguously indicate the capacity to produce lignin-like constituents prior to the evolution of vascular plants. However vanillin is the major and sometimes only oxidation product of lignins derived from gymnosperms (Hegnauer, 1962-1992). The typical byproducts of vanillin often are alkylbenzaldehydes, which have not been investigated in this study due to their low abundances attributed to an enhanced volatility.

Nevertheless the boiling points of alkylbenzaldehydes are not supposed to differ significantly from the one of vanillin. The high proportions of vanillin in many samples therefore may indicate a contribution of gymnospermous-like lignin to their organic matter.

7.6.2 Individual Compounds of Enhanced Chemotaxonomic Significance

Compounds that can be attributed to the presence of gymnosperms in general are of little value, due to most of the organic matter normally investigated postdates their evolutionary appearance. However, for the investigated samples markers that can be unambiguously attributed to specific gymnosperms are of significance. Although it is presumable that gymnosperms have evolved somewhen in the Carboniferous, it is common agreement that at least conifers have evolved in the Late Carboniferous (Hart, 1987; Kerp, 1996).

Although the presence of lignin is no exclusive characteristic of gymnosperms, the relative amounts of the three basic constituents of lignin, coumaryl alcohol, coniferyl alcohol and sinapyl alcohol are supposed to differ for gymnosperms in comparison to their precursors (Hegnauer, 1962-1992). The three constituents differ in relative contents of oxygen. A relative increase of oxygen in lignin of gymnosperms is attributed to coniferyl alcohol being the predominant constituent, whereas for angiosperms the contents of oxygen are often more elevated due to the high proportions of sinapyl alcohol (Hegnauer, 1962-1992; Gottlieb, 1989).

Besides monohydroxy- and monomethoxy-benzoic acids, which were only present in samples of the Carboniferous, 4-hydroxy-3-methoxy- and 3,4-dimethoxybenzoic acid were present in samples extending the time range from Late Devonian to Permian and the maturity range from 0.32 to 1.26% R_r. The two acids normally result from the CuO oxidation of gymnospermous lignin. They are also supposed to be products within the biodegradation of this lignin. However the organic matter of the investigated samples has neither been subject to strong biodegradation nor has it been oxidised during sample preparation. In correspondence to the findings of

Stefanova and Disnar (2000) and Mejanelle *et al.* (1997) the compounds, however, may also be present as free constituents in organic matter and especially resinous secretions. Their relative proportions correlate to the amounts of hydroxy- and methoxybenzoic acids and may therefore indicate a contribution from gymnospermous lignin. Although both compounds are strongly related to coniferyl alcohol, 3,4-dimethoxybenzoic acid normally is present in higher amounts than 4-hydroxy-3-methoxybenzoic acid. This however may result from the enhanced thermal stability of the second methoxy group in comparison to the hydroxy group. The proportions of 4-hydroxy-3-methoxy- to 3,4-dimethoxybenzoic acid show no dependence on the maturity. Nevertheless the relative concentration of the two compounds compared to the amounts of dehydroabietic acid is relatively enhanced for samples from Westphalian C and for few of the Lower Carboniferous samples (Fig. 7.41). While this for the Lower Carboniferous samples may be due to their thermodynamic stabilities, for coals from the Westphalian C this in correspondence to the findings of Gottlieb (1989), may indicate the relative enhancement of coniferyl alcohols in lignin in this period. The low amounts for samples of the Permian may account to the depleted proportions of terrigenous organic matter for these samples or their enhanced thermal maturity.

The presence of dehydroabietic acid normally is attributed to resins derived from gymnosperms. However the detection of this compound in most of the samples extending from Devonian to Permian contradicts this unambiguous origin. Due to the evolution of gymnosperms attributed to the Carboniferous, the presence of dehydroabietic acid in samples predating this event, indicates, that the precursors of gymnosperms have been capable to synthesize this compound. Therefore its presence actually may be of little significance. Nevertheless the absence of dehydroabietic acid in organic matter from South China may indicate the separate evolution for its flora. The presence of dehydroabietic acid in the *Sigillaria* is unexpected and it is insecure, whether the presence results from contamination, i.e. impregnation, or if this plant has been capable to synthesize the compound.

The abundance of gymnosperm markers in samples that predate their evolution has already been found for tetracyclic diterpanes of the phyllocladane type. While these compounds were only present in the aliphatic hydrocarbon fraction

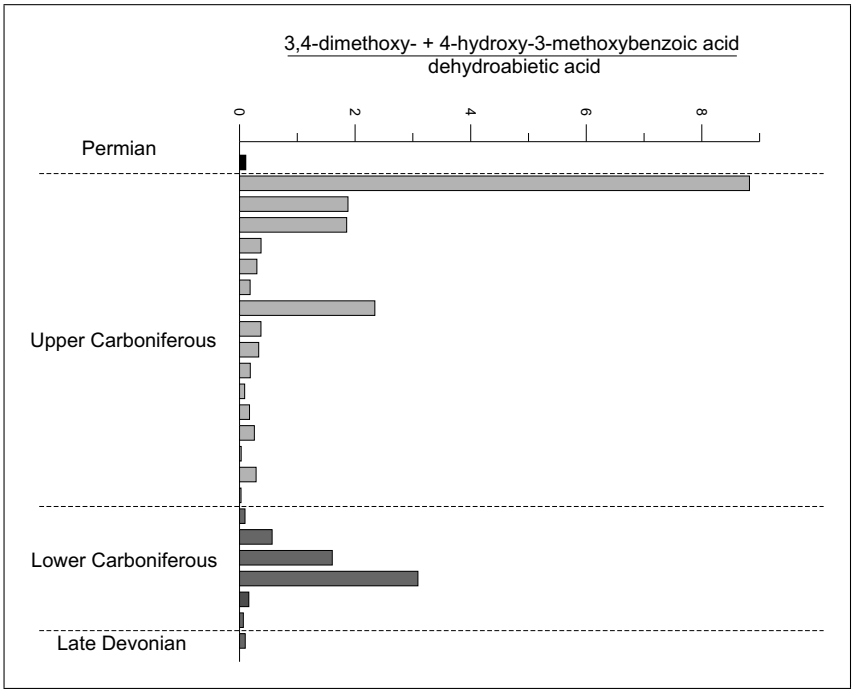

Figure 7.41: Bar diagram showing the ratio of 3,4-dimethoxy- and 4-hydroxy-3-methoxybenzoic acid to dehydroabietic acid

of the low maturity samples from the Moscow Basin, 6-isopropyl-2-methyl-1(4-methylpentyl)naphthalene is supposed to be an aromatic degradation product of phyllocladane. Due to the carboxylic acid group in abietic acid, a breakdown of the A-ring does not occur in the latter compound and in corresponding resinous acids. This therefore supports the tentative attribution of 6-isopropyl-2-methyl-1(4-methylpentyl)naphthalene to phyllocladanes (Ellis *et al.*, 1996). Compounds of the phyllocladane, ent-beyerane and kaurane type are normally attributed to gymnosperms. Nevertheless, Disnar and Harouna (1994) found these compounds in organic matter predating the evolution of gymnosperms. The authors suggested, that they therefore have been constituents of the ancestors of gymnosperms. However, compounds of the phyllocladane type are not present in Pinaceae. This indeed would indicate that the evolution of conifers of the Pinaceae type and other conifers separated early. This has been suggested by many authors (Hart, 1987; Bowe *et al.*, 2000; Chaw *et al.*, 2000; Schmidt and Schneider-Poetsch, 2002) and the observations made here would indicate that this separation at least occurred in the Early Carboniferous. Besides the presence of phyllocladane derived ip-iHMN,

the presence of retene and enhanced proportions of 1,2,5-trimethylnaphthalene do indicate an enhanced contribution of gymnosperm derived organic matter. The strong correlation of 1,7-dimethylphenanthrene and 1,2,5-trimethylnaphthalene for immature samples indicates, that agathic acid is a potential precursor. The correlation is not that strong for samples of enhanced maturity. This however can be attributed to the fact, that especially 1,7-dimethylphenanthrene may also be derived from the degradation of retene. While normally correlation between retene and the tentative 7-ethyl-1-methyl-phenanthrene has been strong, this does not account for more mature samples. The strong correlation between retene and 1,7-dimethylphenanthrene for these samples indicates that the corresponding 7-ethyl-1-methylphenanthrene may be subject to fast breakdown at elevated temperatures while retene may be still released at the same time. Although the correlation and relationship of the compounds is rather complex, they are all suggested to originate from constituents of resins attributed to gymnosperms.

Another indication for gymnosperms throughout the whole Carboniferous is the presence of the monoterpenes thymol and carvacrol in many of the samples. Although the quantitative significance of this compounds due to their enhanced volatility is limited, they are known to be important constituents of gymnosperm derived resins. High amounts of the two compounds have been preferentially attributed to Cupressaceae (Frohne, 1992). Besides these two monoterpenes, strained compounds like borneol, isoborneol and fenchyl alcohol in fossil resins are often linked to resin acids via esterification. The preservation of these compounds in many of the samples may therefore result from their protection due to the bonding into a macromolecular matrix. In ambers, abietic acid and fenchyl alcohol, borneol etc. are linked via esterification and therefore may retain their original configuration (Tauber, 2000). The occurrence of intact monoterpene alcohols and ketones in samples of the Paleozoic, except for thymol and carvacrol is reported for the first time in this study. Although their quantitative behaviour is of little value, their presence indicates, that plants have already been capable to synthesize functionalised monoterpenes. Monoterpenes present in algae normally are aliphatic hydrocarbons and possess no functionalised groups.

A generally accepted age-specific marker is 18α-oleanane. 18α-Oleanane is a conversion product of β-amyrin, present in angiosperms. Although oleananes have been found in samples that predate the Cretaceous, concentrations have been reported to increase significantly when angiosperms evolved (Moldowan *et al.*, 1994). The presence of oleananes in samples that predate the evolution of angiosperms has been attributed to a possible separate lineage leading to the angiosperms or to a related plant type, that possessed the availability to synthesize oleanane precursors (Moldowan *et al.*, 1994). Indeed Tori *et al.* (1995) found a 18δ-oleanane-type triterpene ester in an unidentified liverwort of the *Frullania* species. Although compounds of the oleanane-type normally are not found in liverworts, the presence of this compound in a liverwort from South America shows that these plants may have the capacity to synthetisize these so-called biomarkers of angiosperms. Compounds of the oleanane type were not present in any of the investigated samples in this study. Although oleanane has been detected in samples of the Jurassic (Matsumoto *et al.*, 1987) and even the Pennsylvanian (Moldowan *et al.*, 1994), its absence in the investigated samples corresponds well to the fact, that angiosperms had not yet evolved in the Upper Paleozoic.

In contrast 1,2,7-trimethylnaphthalene, also attributed to precursors of the oleanane type (Püttmann and Villar, 1987; Strachan *et al.*, 1988; Forster *et al.*, 1989) was generally present. For none of the samples 1,2,7-trimethylnaphthalene showed an extraordinary low or high proportion but normally strongly correlated to most of the other trimethylnaphthalenes. The formation of 1,2,7-trimethylnaphthalene may therefore have proceeded via isomerisation reactions (van Aarssen *et al.*, 1999). In contrast an elevated importance of isomerisation reactions does not correspond to the observations in the studies of Strachan *et al.* (1988), where high amounts of 1,2,7-trimethylnaphthalene compared to 1,3,7-trimethylnaphthalene distinguished samples of the Cretaceous and younger from those, where oleanane and its precursors were generally absent. Another specific precursor of 1,2,7-trimethylnaphthalene, besides triterpenes of the oleanane type, however yet is unknown.

The plot proposed by Strachan *et al.* (1988) for the samples investigated in this study shows, that 1,2,5- and 1,2,7-trimethylnaphthalene are present in relatively

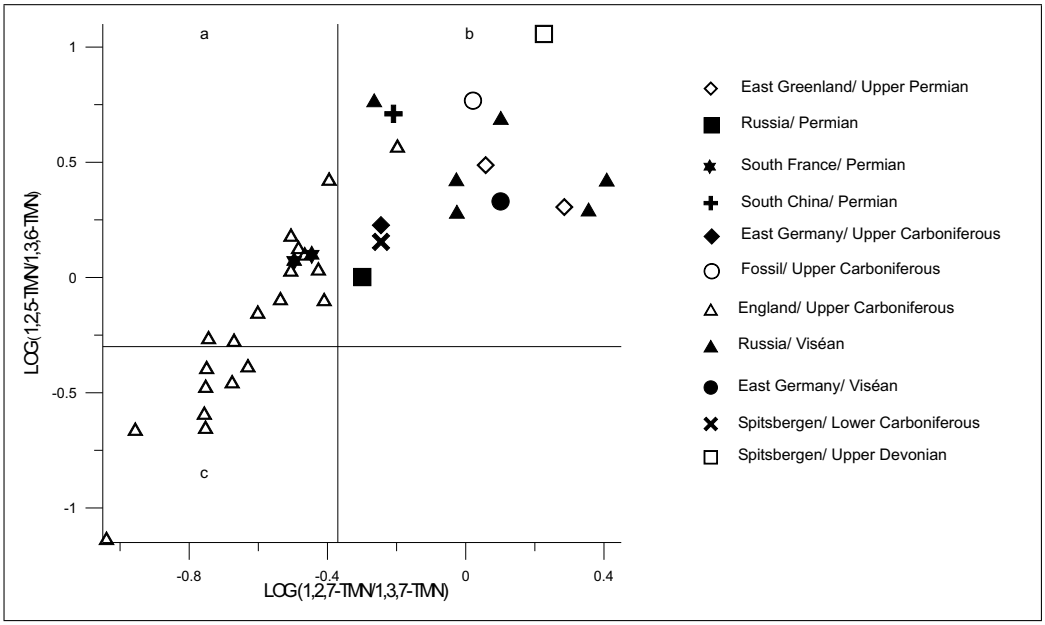

Figure 7.42: Cross plot of the logarithms of the ratios 1,2,7-TMN/1,3,7-TMN to 1,2,5-TMN/1,3,6-TMN and benchmark values for the ratios according to Strachan *et al.* (1988)

high proportions in many samples (Fig. 7.42). Outliers are the Upper Carboniferous samples from England and the Permian samples from South France only (Fig. 7.42). These samples are characterised by relatively high concentrations of 1,2,5-trimethylnaphthalene only, or low proportions of both compounds, respectively (Fig. 7.42). The relative enhanced proportions of both isomers in accordance with the most stable isomerisation products, for many samples strongly contradict the hypothesis that 1,2,7-trimethylnaphthalene is a marker for angiosperms. Either the significance of the ratio (1,2,7-/ 1,3,7-trimethylnaphthalene) is questionable, or 1,2,7-trimethylnaphthalene may originate from another natural source, yet unknown. However, a strong correspondence between the relative amounts of cadalene and 1,2,7-trimethylnaphthalene indeed may indicate a specific source.

Both plots, the one of Strachan *et al.* (1988) and the one of this study (Fig. 7.42) are characterised by a comparable distribution of samples. However, in contrast to the samples of Strachan *et al.* (1988) none of the samples investigated in this study has been deposited in times where angiosperms had already evolved. Whereas the authors distinguished samples originating from the Cretaceous and younger from those that originate from earlier times by enhanced proportions of

1,2,7-trimethylnaphthalene, the samples investigated in this study do not correspond to this characteristic. Additionally 1,2,5- and 1,2,7-trimethylnaphthalene have not been characterised by a strong correlation for the majority of the samples. Although this may result from the magnitude of contribution from different precursors for 1,2,5-trimethylnapthalene (agathic acid, manool, C_{29}-monoaromatic-8,14-secohopanoids), the significance of 1,2,7-trimethylnaphthalene as a potential age specific biomarker is questionable. It should be recognised that due to the studies of Tori *et al.* (1995) a strong correlation might also point to a contribution of organic matter from liverworts. Some of the Cretaceous samples examined by Strachan *et al.* (1988) showed no significantly enhanced proportions of 1,2,7-trimethylnaphthalene in comparison to other isomers. In this study 1,2,7-trimethylnaphthalene in contrast to 1,2,5-trimethylnaphthalene never is predominant, but often is present in similar amounts like other isomers. This indicates, that concentrations of 1,2,7-trimethylnaphthalene are significantly more influenced by maturity than has been suggested by Strachan *et al.* (1988). The significance of 1,2,7-trimethylnaphthalene as a marker for angiosperms therefore is insecure. The relative amounts of the compound depend on thermal maturities. If concentrations are not significantly enhanced compared to other trimethylnaphthalenes it probably can not be regarded as a biomarker of angiosperms.

8 Summary and Conclusions

The present investigations on the occurrence and relative amounts of low molecular weight compounds provide important information on both the evolution of land plants and on abiotic chemical reactions occurring in sediments. The observations base on the composition of aromatic hydrocarbons and functionalised low molecular weight compounds. Bulk results and the composition of aliphatic hydrocarbons in contrast served to estimate the influences of environmental factors, i.e. origin of the organic matter, thermal history and early sedimentary redox conditions on the composition of low molecular weight compounds in the samples.

The hypothesis that alkyldibenzofurans are terrestrial biomarkers (Radke *et al.*, 2000) is supported in this thesis. The compounds show low correlations indicating contribution from specific sources. This is more apparent for terrigenous samples than for samples consisting predominantly of type I kerogen. Most significantly 1-methyldibenzofuran often is characterised by weakest correlation. The compound therefore may indeed be a specific marker of lichens.

Both phenylnaphthalenes and benzo[*b*]naphthofurans in this thesis were assigned to be terrestrial markers. For 1-phenylnaphthalenes it is suggested that they originate from lignans and are easily transformed into 2-phenylnaphthalenes due to thermal stress. The origin of benzo[*b*]naphthofurans is more insecure, it is proposed that they are condensation products of compounds showing an ubiquitous terrestrial origin.

Specific alkylnaphthalenes and alkylphenanthrenes are generally accepted to be terrestrial markers of higher plants. This for example does account for retene, its degradation products 7-ethyl-1-phenanthrene and 1,7-dimethylphenanthrene,

cadalene, 1,2,5- and 1,2,7-trimethylnaphthalene and 6-isopropyl-2-methyl-1-(4-methylpentyl)naphthalene. All of these compounds were present in the investigated samples. However it is presumed in this thesis that the original constitution is more apparent for alkylphenanthrenes due to a later releasement from kerogen and therefore the later proceeding of isomerisation reactions. While the significance of 1,2,7-trimethylnaphthalene as a marker of angiosperms based on the observations made in this thesis is limited, the presence of 6-isopropyl-2-methyl-1-(4-methylpentyl)naphthalene may indicate that Pinaceae became a separated line of conifers early in the Late Paleozoic.

The occurrence of monoterpene alcohols (borneol, fenchyl alcohol) and ketones (camphor, verbenone) in many of the investigated samples of the Paleozoic is reported for the first time. Although no systematics on their appearance in individual samples could be assigned, their presence in general shows that already Devonian plants were capable to synthesize these compounds.

4-Hydroxy-3-methoxybenzoic acid and 3,4-dimethoxybenzoic acid are degradation products of lignin originating from gymnosperms. The high amounts of these compounds in samples of the Westphalian C may point to an emerge of gymnosperms at this time. Long chain *n*-fatty acids were only present in three immature samples. It therefore is presumed that higher plants of the Late Paleozoic were not generally capable to produce these compounds.

It is proposed in this thesis that 1,2,8-trimethylnaphthalene is a biomarker. The compound is highly abundant in samples which often show low amounts of terrestrial organic matter but also in the *Sigillaria*. 1,2,8-Trimethylnaphthalene may originate from tetracyclic triterpenoids of the dammarane type or from plant steroids.

With regard to abiotic chemical reactions occurring in the sediments, it is suggested in this thesis, that alkylfluorenes are easily oxidised to alkylfluoren-9-ones and alkylnaphthalenes and -phenanthrenes to the corresponding ketones and aldehydes. The formation of alkylnaphthalenecarboxylic acids and alkylphenanthrenecarboxylic acids in contrast requires thermal stress, while at a certain magnitude of thermal stress destruction of these carboxylic acids again proceeds.

Further it is proposed, that alkylbiphenyls, alkylfluorenes, alkylcarbazoles and alkylbenzothiophenes are formed randomly in sediments. Alkylbiphenyls are instable due to their low proportions in general and their absence in more mature samples. Alkylfluorenes and alkylcarbazoles are formed early in the sedimentary record and isomerisation of individual isomers seems to occur immediately after formation. This hypothesis base on the little variations in the composition of isomers for individual samples. For alkyldibenzothiophenes in contrast the formation of precursors probably occurs early while their formation and especially isomerisation reactions proceed due to thermal stress at higher thermal maturities.

Alkylxanthones have only been present in few samples. Based on these fact it was not possible to estimate whether these compounds were formed randomly due to elevated maturities or whether they may have a specific terrestrial origin.

Bibliography

Achari, R. G., Shaw, G., Holleyhead, R., 1973. Identification of ionene and other carotenoid degradation products from the pyrolysis of sporopollenins derived from some pollen exines, a spore coal and the green river shale. Chemical Geology 12, 229–234.

Ahmed, M., Smith, J. W., George, S. C., 1999. Effects of biodegradation on Australian Permian coals. Organic Geochemistry 30, 1311–1322.

Aitzetmüller, K., Vosmann, K., 1998. Cyclopropenoic fatty acids in gymnosperms: The seed oil of *Welwitschia*. Journal of the American Oil Chemists Society 75, 1761–1765.

Alekseev, A. S., Kononova, L. I., Nikishin, A. M., 1996. The Devonian and Carboniferous of the Moscow Syneclise (Russian Platform): stratigraphy and sea-level changes. Tectonophysics 268, 149–168.

Alexander, G., Hazai, I., Grimalt, J., Albaigés, J., 1987. Occurrence and transformation of phyllocladanes in brown coals from Nograd Basin, Hungary. Geochimica et Cosmochimica Acta 51, 2065–2073.

Alexander, R., Baker, R. W., Kagi, R. I., Warton, B., 1994. Cyclohexylbenzenes in crude oils. Chemical Geology 113, 103–115.

Alexander, R., Bastow, T. P., Fisher, S. J., Kagi, R. I., 1995. Geosynthesis of organic compounds: II. Methylation of phenanthrene and alkylphenanthrenes. Geochimica et Cosmochimica Acta 59, 4259–4266.

Alexander, R., Bastow, T. P., Kagi, R. I., Singh, R. K., 1992. Identification of 1,2,2,5-Tetramethyltetralin and 1,2,2,3,4-Pentamethyltetralin as Racemates in Petroleum. Journal of the Chemical Society, Chemical Communications 1906, 1712–1714.

Alexander, R., Cumbers, K. M., Kagi, R. I., 1986a. Alkylbiphenyls in ancient sediments and petroleums. Organic Geochemistry 10, 841–845.

Alexander, R., Fisher, S. J., Kagi, R. I., 1988. 2,3-Dimethylbiphenyl: Kinetics of its cyclisation reaction and effects of maturation upon its relative concentration in sediments. Organic Geochemistry 13, 833–837.

Alexander, R., Kagi, R. I., Rowland, S. J., Sheppard, P. N., Chirila, T. V., 1986b. The effects of thermal maturity on distributions of dimethylnaphthalenes and trimethylnaphthalenes in some ancient sediments and petroleums. Geochimica et Cosmochimica Acta 49, 385–395.

Alexander, R., Kagi, R. I., Sheppard, P. N., 1983. Relative abundance of dimethylnaphthalene isomers in crude oils. Journal of Chromatography 267, 367–372.

Anderson, J. M., Anderson, H. M., Archangelsky, S., Bamford, M., Chandra, S., Dettmann, M., Hill, R., Mcloughlin, S., O, R., 1999. Patterns of Gondwana plant colonisation and diversification. Journal of African Earth Sciences 28, 145–167.

Anderson, K. B., 1994. The nature and fate of natural resins in the geosphere-IV. Middle and Upper Cretaceous amber from the Taimyr Peninsula Siberia-evidence for a new form of polylabdanoid of resinite and revision of the classification of Class I resinites. Organic Geochemistry 21, 209–212.

Anderson, K. B., Botto, R. E., 1993. The nature and fate of natural resins in the geosphere- III. Re-evaluation of the structure and composition of *Highgate Copalite* and *Glessite*. Organic Geochemistry 20, 1027–1038.

Anderson, K. B., Winans, R. E., 1991. Nature and Fate of Natural Resins in the Geosphere. 1. Evaluation of Pyrolysis-Gas Chromatography/Mass Spectrometry for the Analysis of Natural Resins and Resinites. Analytical Chemistry 63, 2901–2908.

Aquino Neto, F. R., Trendel, J. M., Restle, A., Connan, J., Albrecht, P. A., 1983. Advances in Organic Geochemistry, chapter Occurrence and Formation of Tricyclic and Tetracyclic Terpanes in Sediments and Petroleums. John Wiley & Sons Limited, 659–667.

Armstrong, D. W., Zhou, E. Y., Zukowski, J., Kosmowska-Ceranowicz, B., 1996. Enantiomeric Composition and Prevalence of some Bicyclic Monoterpenoids in Amber. Chirality 8, 39–48.

Arpino, P. J., Ignatiadis, I., Rycke, G., 1987. Sulphur-containing polynuclear aromatic hydrocarbons from petroleum: Examination of their possible statistical formation in sediments. Journal of Chromatography 390, 329–348.

Bakel, A. J., Philp, R. P., 1990. Advances in Organic Geochemistry 1989, chapter The distribution and quantitation of organonitrogen compounds in crude oils and rock pyrolysates. Pergamon Press, London, 353–367.

Baker, E. W., Louda, J. W., 1986. Biological markers in the sedimentary record, chapter Porphyrins in the geological record. Elsevier, Amsterdam, 125–225.

Bakr, M. M. Y., Wilkes, H., 2002. The influence of facies and depositional environment on the occurrence and distribution of carbazoles and benzocarbazoles in crude oils: a case study from the Gulf of Suez, Egypt. Organic Geochemistry 33, 561–580.

Barnes, C. R., 1999. Paleooceanography and paleoclimatology: an earth system perspective. Chemical Geology 161, 17–35.

Bastow, T. P., van Aarssen, B. G. K., Alexander, R., Kagi, R. I., 1999. Biodegradation of aromatic land-plant biomarkers in some Australian crude oils. Organic Geochemistry 30, 1229–1239.

Behar, F. H., Albrecht, P., 1984. Correlations between carboxylic acids and hydrocarbons in several crude oils. Alteration by biodegradation. Organic Geochemistry 6, 597–604.

Bennett, B., Abbott, G. D., 1999. A natural pyrolysis experiment- hopanes from hopanoic acids? Organic Geochemistry 30, 1509–1516.

Bennett, B., Bowler, B. F. J., Larter, S. R., 1996. Determination of C_0-C_3 Alkylphenols in Crude Oils and Waters. Analytical Chemistry 68, 3697–3702.

Bennett, B., Larter, S. R., 2000. The isolation, occurrence and origin of fluorenones in crude oils and rock extracts. Organic Geochemistry 31, 117–126.

Bennett, G. J., Lee, H.-H., 1989. Xanthones from guttiferae. Phytochemistry 28, 967–998.

Birkelund, T., Perch-Nielsen, K., 1976. Late Paleozoic - Mesozoic evolution of central East Greenland. The Geological Survey of Greenland, 305–337.

Birkenmajer, K., 1981. The ocean basins and margins. volume 5: The Arctic Ocean, chapter The geology of Svalbard, the western part of the Barents Sea, and the continental marin of Scandinavia. Plenum Press, New York, 265–329.

Bode, H., 1930. Über die Algen der Moskauer Kohle. Braunkohle 1930, 1–6.

Bode, H., Feist, G., 1928. Beiträge zur Kenntnis der Moskauer Kohle. Braunkohle 27, 1070–1087.

Borrego, A. G., Blanco, C., Püttmann, W., 1997. Geochemical significance of the aromatic hydrocarbon distribution in the bitumens of the Puertollano oil shales, Spain. Organic Geochemistry 26, 219–228.

Borwitzky, H., Schomburg, G., 1979. Separation and identification of polynuclear aromatic compounds in coal tar by using glass capillary chromatography including combined gas chromatography-mass spectrometry. Journal of Chromatography 170, 99–124.

Bowe, L. M., Coat, G., dePamphilis, C. W., 2000. Phylogeny of seed plants based on all three genomic compartments: Extant are monophyletic and gnetales closest relatives are conifers. Proceedings of the Academy of Sciences (USA) 97, 4092–4097.

Bowler, B. F. J., Larter, S. R., Clegg, H., Wilkes, H., Horsfield, B., Li, M., 1997. Comment on liquid chromatographic separation schemes for pyrrole and pyridine nitrogen aromatic heterocyclic fractions from crude oils suitable for rapid charactersation of geochemical samples. Analytical Chemistry 69, 3128–3129.

Brassell, S. C., 1985. Molecular changes in sediment lipids as indicators of systematic early diagenesis. Philosophical Transactions of the Royal Society A 315, 57–75.

Budzinski, H., Garrigues, P., Connan, J., Devillers, J., Domine, D., Radke, M., Oudin, J. L., 1995. Alkylated phenanthrene distributions as maturity and origin indicators in crude oils and rock extracts. Geochimica et Cosmochimica Acta 59, 2043–2056.

Budzinski, H., Garrigues, P., Radke, M., Connan, J., Rayez, J. C., Rayez, M. T., 1993. Use of molecular modeling as a tool to evaluate thermodynamic stability of alkylated polycyclic aromatic hydrocarbons. Energy & Fuels 7, 505–511.

Budzinski, H., Nadalig, T., Raymond, N., Ni´Matuzahroh, Gilewicz, M., 2000. Evidence of two metabolic pathways for degradation of 2-methylphenanthrene by *Shingomonas* Sp. Strain (2MPI). Environmental Toxicology and Chemistry 19, 2671–2677.

Cardellina, J. K., Kirkup, M. P., Moore, R. E., Mynderse, J. S., Asimmons, C. J., 1979. Hyellazole and chlorohyellazole, two novel carbazoles from the blue-green algae *Hyella caespitosa* Born. et Flah. Tetrahedron Letters 51, 4915–4916.

Carman, R. M., Craig, W., 1971. Diterpenoids XXVII. The selenium dehydrogenation of manool. Aust. J. Chem. 24, 361–370.

Casellas, M., Grifoll, M., Bayona, J. M., Solanas, A. M., 1997. New Metabolites in the Degradation of Fluorene by *Arthrobacter* sp. Strain F101. Applied and Environmental Microbiology 63, 819–826.

Chaffee, A. L., Fookes, C. J. R., 1988. Polycyclic aromatic hydrocarbons in Australian coals-III. Structural elucidation by proton nuclear magnetic resonance spectroscopy. Organic Geochemistry 12, 261–271.

Chaffee, A. L., Johns, R. B., 1983. Polycyclic aromatic hydrocarbons in Australian coals. I. Angularly fused pentacyclic tri- and tetraaromatic components of Victorian brown coals. Geochimica et Cosmochimica Acta 47, 2141–2155.

Chakhmakhchev, A., Suzuki, M., Takayama, K., 1997. Distribution of alkylated dibenzothiophenes in petroleum as a tool for maturity assessments. Organic Geochemistry 26, 483–490.

Chaloner, W. G., Meyen, S. V., 1973. Atlas of Palaeobiogeography, chapter Carboniferous and Permian Floras of the Northern Continents. Elsevier, Amsterdam, 169–186.

Chaw, S.-M., Parkinson, C. L., Cheng, Y., Vincent, T. M., Palmer, J. D., 2000. Seed plant phylogeny inferred from all three plant genomes: Monophyly of extant gymnosperms and origin of gnetales from conifers. Proceedings of the National Academy of Sciences (USA) 97, 4086–4091.

Chen, J., Summons, R. E., 2001. Complex patterns of steroidal biomarkers in Tertiary lacustrine sediments of the Biyang Basin, China. Organic Geochemistry 32, 115–126.

Christiansen, F. G., Dam, G., Piasecki, S., Stemmerik, L., 1992. Generation, Accumulation and Production of Europe´s Hydrocarbons II, chapter A Review of Upper Paleozoic and Mesozoic Source Rocks from Onshore East Greenland. Special Publication of the European Association of Petroleum Geoscientists, 151–161.

Christiansen, F. G., Piasecki, S., Stemmerik, L., Telnæs, N., 1993. Depositional Environment and Organic Geochemistry of the Upper Permian Ravnefjeld Formation Source Rock in East Greenland. The American Association of Petroleum Geologists Bulletin 77, 1519–1937.

Clegg, H., Horsfield, B., Wilkes, H., Sinninghe-Damste, J., Koopmans, M. P., 1998a. Effect of artificial maturation on carbazole distributions, as revealed by the hydrous pyrolysis of an organic-sulphur-rich source rock (Ghareb Formation, Jordan). Organic Geochemistry 29, 1953–1960.

Clegg, H., Wilkes, H., Horsfield, B., 1997. Carbazoles distributions in carbonate and clastic source rocks. Geochimica et Cosmochimica Acta 61, 5335–5345.

Clegg, H., Wilkes, H., Oldenburg, T., Santamaria-Orozco, D., Horsfield, B., 1998b. Influence of maturity on carbazole and benzocarbazole distributions in crude oils and source rocks from the Sonda de Campeche, Gulf of Mexico. Organic Geochemistry 29, 183–194.

Costa Neto, C., Maçaira, A. M. P., Pinto, R. C. P., Nakayama, H. T., Cardoso, J. N., 1980. New analytical approaches to organic geochemistry: solid phase functional group extraction for bitumens and functional markers for kerogens. Pergamon Press, Oxford, 249–263.

Courel, L., 1989a. Peat and Coal: Origin, Facies, and Depositional Models, volume 12, chapter Organics versus clastics: conditions necessary for peat (coal) development. Elsevier Science Publishers B. V., Amsterdam, 193–207.

Courel, L., 1989b. Sedimentation in a Synorogenic Basin Complex: the Upper Carboniferous of Northwest Europe, chapter Intramontane Stephanian and Permian coal basins of the Frenche Massif Central; new sedimentological data. Blackie, Glasgow and London, 255–263.

Cozzarelli, I. M., Eganhouse, R. P., Baedecker, M. J., 1990. Transformation of Monoaromatic Hydrocarbons to Organic Acids in Anoxic Groundwater Environment. Environmental Geological Water Sciences 16, 135–141.

Cranwell, P. A., 1974. Monocarboxylic acids in lake sediments: Indicators, derived from terrestrial and aquatic biota, of paleoenvironmental trophic levels. Chemical Geology 14, 1–14.

Crowley, T. J., Baum, S. K., 1995. Reconciling Late Ordovician (440 MA) glaciation with very high (14X) CO_2 levels. Journal of Geophysical Research 100, 1093–1101.

Cullmann, F., Schmidt, A., Schuld, F., Trennheuser, M. L., Becker, H., 1999. Lignans from the liverworts *Lepidoza incurvata, Chiloscyphus polyanthos* and *Jungermannia exsertifolia* ssp. *cordifolia*. Phytochemistry 52, 1647–1650.

Cumbers, K. M., Alexander, R., Kagi, R. I., 1987. Methylbiphenyl, ethylbiphenyl and dimethylbiphenyl isomer distributions in some sediments and crude oils. Geochimica et Cosmochimica Acta 51, 3105–3111.

Davies, D. I., Waring, C., 1968. Cyclisation reactions involving the oxdation of carboxylic acids with lead tetra-acetate. PartIV. The oxidation of *o*-Benzoyl- and *o*-benzyl-benzoic acids. Journal of the Chemical Society (C) , 2337–2338.

Davin, L. B., Lewis, N. G., 2000. Dirigent proteins and dirigent sites explain the mystery of spcificity of radical precursor coupling in lignan and lignin biosynthesis. Plant Physiology 123, 453–461.

Day, W. C., Erdman, J. G., 1963. Ionene: a thermal degradation product of β-carotene. Science 141, 808.

de Leeuw, J. W., Baas, M., 1986. Biological markers in the sedimentary record, chapter Early-stage diagenesis of steroids. Elsevier, Amsterdam, 101–123.

Disnar, J. R., Harouna, M., 1994. Biological origin of tetracyclic diterpanes, *n*-alkanes and other biomarkers found in Lower Carboniferous Gondwana coals (Niger). Organic Geochemistry 21, 143–152.

Djerassi, C., 1981. Recent studies in the marine sterol field. Pure and Applied Chemistry 53, 873–890.

Djerassi, C., Theobald, N., Kokke, W. C. M. C., Pak, C. S., Karlson, R. M. K., 1979. Recent progress in the marine sterol field. Pure and Applied Chemistry 51, 1815–1828.

Dorbon, M., Schmitter, J. M., Garrigues, P., Ignatiadis, I., Evald, M., Arpino, P., Guiochon, G., 1984. Distribution of carbazole derivatives in petroleum. Organic Geochemistry 7, 111–120.

Douglas, A. G., Mair, B. J., 1965. Sulfur: Role in Genesis of Petroleum. Science 147, 499–501.

Dutta, T. K., Selifonov, S. A., Gunsalus, I. C., 1998. Oxidation of methyl-substituted naphthalenes: Pathways in a versatile *spingomonas paucimobilis* strain. Applied and Environmental Microbiology 64, 1884–1889.

Dzou, L. I. P., Noble, R. A., Senflte, J. T., 1995. Maturation effects on absolute biomarker concentrations in a suite of coals and associated vitrinite concentrates. Organic Geochemistry 23, 681–697.

Edwards, D., Feeham, J., 1980. Records of *Cooksonia*-type sporangia from late Wenlock strata in Ireland. Nature 287, 41–42.

Eglington, G., Hunnemann, D. H., Douraghi-Zadeh, K., 1968. Gas chromatographic-mass spectrometric studies of long-chain hydroxy acids-II. The hydroxy acids and fatty acids of a 5000-year-old lacustrine sediment. Tetrahedron 24, 5929–5941.

Ellis, L., Singh, R. J., Alexander, R., Kagi, R. I., 1996. Formation of isohexyl alkylaromatic hydrocarbons from aromatization-rearrangement of triterpenoids in the sedimentary environment: A new class of biomarkers. Geochimica et Cosmochimica Acta 60, 4747–4763.

Epistalié, J., Bordenave, M. L., 1992. Applied Petroleum Geochemistry, chapter Tools for source-rock routine analysis. Technip, Paris, 237–261.

Eriksson, M., Dalhammer, G., Borg-Karlson, A. K., 2000. Biological degradation of selected hydrocarbons in an old PAH/creosote contamined soil from a gas work site. Applied Microbiology Biotechnology 53, 619–626.

Espistalié, J., 1985. Thermal modelling in sedimentary basins, chapter Use of T_{max} as a maturation index for different types of organic matter. Edit. Technip., Paris, 475–496.

Espitalié, J., Laporte, J. L., Madec, M., Marquis, F., Leplat, P., Paulet, J., Boutefeu, A., 1977. Méthode rapide de caractérisation des roches mères, de potentiel pétrolier et de leur degrè d evolution. Revue de l Institut Français du Pétrole 32, 23–42.

Falcon-Lang, H. J., 1999. The Early Carboniferous (Asbian-Brigantian) Seasonal Tropical Climate of Northern Britain. PALAIOS 14, 116–126.

Farrimond, P., Bevan, J. C., Bishop, A. N., 1996. Hopanoid hydrocarbon maturation by an igneous intrusion. Organic Geochemistry 25, 149–164.

Farrimond, P., Head, I. M., Innes, H. E., 2000. Environmental influence on the biohopanoid composition of recent sediments. Geochimica et Cosmochimica Acta 64, 2985–2992.

Forster, P. G., Alexander, R., Kagi, R. I., 1989. Identification and analysis of tetramethylnaphthalenes in petroleum. Journal of Chromatography 483, 384–389.

Fortnagel, P., Harms, H., Wittich, R.-M., Francke, W., Krohn, S., Meyer, H., 1989. Cleavage of dibenzofuran and dibenzodioxin ring systems by a *pseudomonas* bacterium. Naturwissenschaften 76, 222–223.

Fortnagel, P., Harms, H., Wittich, R.-M., Krohn, S., Meyer, H., Sinnwell, V., Wilkes, H., Francke, W., 1990. Metabolism of Dibenzofuran by *Pseudomonas* sp.Strain HH69 and the Mixed Culture HH27 . Applied and Environmental Microbiology 56, 1148–1156.

Frohne, D., 1992. Systematik des Pflanzenreichs: unter besonderer Berücksichtigung chemischer Merkmale und pflanzlicher Drogen. 4 edition. Gustav Fischer Verlag, Stuttgart, Germany.

Frolov, Y. B., Smirnov, M. B., Vanyukova, N. A., Sanin, P. I., 1989. Carbazoles of crude oils. Petroleum Chemistry U.S.S.R. 29, 87–102.

Gallegos, E. J., 1981. Possible Significance of the Relative Concentrations of Terpanes, Terpenes, Steranes, and Cadalene in Six United States Coals. Journal of Chromatographic Science 19, 156–160.

Garon, D., Krivobok, S., Seigle-Murandi, F., 2000. Fungal degradation of fluorene. Chemosphere 40, 91–97.

Garrigues, P., Parlanti, E., Radke, M., Bellocq, J., Willsch, H., Ewald, M., 1987. Identification of alkylphenanthrenes in shale oil and coal by liquid and capillary gas chromatography and high-resolution spectrofluorimetry (Shpol'skii effect). Journal of Chromatography 395, 217–228.

Gensel, P. G., Andrews, H. N., 1987. The evolution of early land plants. American Scientist 75, 478–488.

Gong, C., Hollander, D. J., 1997. Differential contribution of bacteria to sedimentary organic matter in oxic and anoxic environments, Santa Monica Basin, California. Organic Geochemistry 26, 545–563.

Gottlieb, O. R., 1989. The role of oxygen in phytochemical evolution towards diversity. Phytochemistry 28, 2545–2558.

Graham, J. B., Dudley, R., Aguilar, N. M., Gans, C., 1995. Implications of the late Palaeozoic oxygen pulse for physiology and evolution. Nature 375, 117–120.

Graham, L. E., 1985. The origin of the life cycle of land plants. American Scientist 73, 178–186.

Gray, J., 1993. Major Paleozoic land plant evolutionary bio-events. Paleogeography, Paleoclimatology, Paleoecology 104, 153–169.

Gray, J., Shear, W., 1992. Early life on land. American Scientist 80, 444–456.

Greiner, A., Spyckerelle, C., Albrecht, P., 1976. Aromatic hydrocarbons from geologic sources-I. New naturally occurring phenanthrene and chrysene derivatives. Tetrahedron 32, 257–260.

Guion, P. D., Fielding, C. R., 1986. Westphalian A and B Sedimentation in the Pennine Basin. Meeting, University of Keele, U. K. Abstracts, 35–37.

Hallsworth, C. R., Morton, A. C., Claoué-Long, J., Fanning, C., 2000. Carboniferous sand provenance in the Pennine Basin, UK: constraints from heavy mineral and detrital zircon age data. Sedimentary Geology 137, 147–185.

Harborne, J. B., 1973. Phytochemistry, chapter Flavonoids. Van Nostrand Reinhold Company, New York, 344–380.

Hart, J., 1987. A cladistic analysis of conifers: preliminary result. Journal of the Arnold Arboretum 68, 269–307.

Hatcher, P. G., H. E. Lerch, I., Verheyen, T. V., 1989. Coal: Classification, Coalification, Mineralogy, Trace-element Chemistry and Oil and Gas Potential, volume 13, chapter Organic geochemical studies of the transformation of gymnospermous xylem during peatification and coalification to subbituminous coal. Elsevier, Amsterdam, 65–97.

Hayatsu, R., Winans, R. E., Scott, R. G., Moore, L. P., Studier, M. H., 1978a. Characterization of organic acids trapped in coals. Nature 275, 116–118.

Hayatsu, R., Winans, R. E., Scott, R. G., Moore, L. P., Studier, M. H., 1978b. Trapped organic compounds and aromatic units in coals. Fuel 57, 541–548.

Hazai, I., Alexander, G., Székely, T., 1989. Study of aromatic biomarkers in brown coal extracts. Fuel 68, 49–54.

Hedges, J. I., Mann, D. C., 1979. The characterization of plant tissues by their lignin oxidation products. Geochimica et Cosmochimica Acta 43, 1803–1807.

Hegnauer, R., 1962-1992. Chemotaxonomie der Pflanzen. Band I bis X, volume I-X. Birkhäuser, Basel, Stuttgart.

Helm, R. V., Latham, D. R., Ferrin, C. R., Ball, J., 1960. Identification of Carbazole in Wilmington Petroleum through Use of Gas-Liquid Chromatography and Spectroscopy. Analytical Chemistry 32, 1765–1767.

Heppenheimer, H., Steffens, K., Püttmann, W., Kalkreuth, W., 1992. Comparison of resinite-related aromatic biomarker distributions in Creataceous-Tertiary coals from Canada and Germany. Organic Geochemstry 18, 273–287.

Hesse, M., 1974. Progress in mass spectrometry, volume 1, chapter Indolalkaloids. Verlag Chemie, Weinheim, 165–189.

Hinrichs, K.-U., Rullkötter, J., 1997. Terrigenous and marine lipids in Amazon Fan sediments: implications for sedimentological reconstructions. In: Flood, R. D., Piper, D. J. W., Klaus, A., Peterson, L. C. (eds.), Proceeding of Ocean Drilling Program, Scientific Results. Ocean Drilling Program, College Station.2, TX, Pt, 201–211.

Hinrichs, K.-U., Schneider, R. R., Müller, P. J., Rullkötter, J., 1999. A biomarker perspective on paleoproductivity variations in two Late Quarternay sediment sections from the Southeast Atlantic Ocean. Organic Geochemistry 30, 341–366.

Holba, A. G., Tegelaar, E. W., Huizinga, B. J., Moldowan, J. M., Singletary, M. S., McCaffrey, M. A., Dzou, L. I. P., 1998. 24-norcholestanes as age-sensitive molecular fossils. Geology 26, 783–786.

Holliday, D. W., Pattison, J., 1987. Carboniferous Geology of Corbridge and Prudhoe. Technical Report WA/90/13, British Geological Survey.

Horsfield, B., Clegg, H., Wilkes, H., 1998. Effect of maturity on carbazole distributions in petroleum systems: new insights from the Sonda de Campeche, Mexico, and Hils Syncline, Germany. Naturwissenschaften 85, 233–237.

Huang, W.-Y., Menschein, W. G., 1979. Sterols as ecological indicators. Geochimica et Cosmochimica 43, 739–745.

Hughes, W. B., Holba, A. G., Dzou, L. I. P., 1995. The ratios of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum in source rocks. Geochimica et Cosmochimica Acta 59, 3581–3598.

Hussler, G., Connan, J., Albrecht, P., 1984. Novel families of tetra- and hexacyclic hopanoids predominant in carbonate rocks and crude oils, volume 6. Pergamon Press, Oxford, 39–49.

Inaba, T., Suzuki, N., Hirai, A., Sekiguchi, K., Watanabe, T., 2001. Source rock lithology prediction based on oil diacholestane abundaces in the siliceous-clastic Akita sedimentary basin, Japan. Organic Geochemistry 32, 877–890.

Ioppolo, M., Alexander, R., Kagi, R. I., 1992. Identification and analysis of C_0-C_3 phenols in some Australian crude oils. Organic Geochemistry 18, 603–609.

Ioppolo-Armanios, M., Alexander, R., Kagi, R. I., 1994. Identification and origins of isopropylmethylphenols in crude oils. Organic Geochemistry 22, 815–823.

Ioppolo-Armanios, M., Alexander, R., Kagi, R. I., 1995. Geosynthesis of organic compounds: I. Alkylphenols. Geochimica et Cosmochimica Acta 59, 3017–3027.

Jacob, H., 1961. Neuere Ergebnisse der Braunkohlen- und Torf-Petrographie-Gedanken zur Mazeral-Klassifikation. Geologische Rundschau 51, 530–546.

Jones, N. S., 1992. Sedimentology of Westphalian coal-bearing strata and applications to opencast coal mining, west Cumbrian Coalfield, U.K. Ph.D. thesis, Oxford Brookes University.

Kagi, R. I., Alexander, R., Toh, E., 1990. Kinetics and mechanism of the cyclisation reaction of *ortho*-methylbiphenyls. Organic Geochemistry 16, 161–166.

Kapil, R. S., 1971. The Alkaloids, volume 13, chapter The carbazole alkaloids. Academic Press, New York, 273–302.

Karrer, W. (ed.), 1976. Konstitution und Vorkommen der organischen Pflanzenstoffe (exclusive Alkaloide), volume 12. 2 edition. Birkhäuser Verlag, Birkhäuser Verlag, Basel, CH.

Katz, B. J., 1983. Limitations of Rock-Eval pyrolysis for typing organic matter. Organic Geochemistry 4, 195–199.

Kenrick, P., Crane, P. R., 1997. The origin and early evolution of plants on land. Nature 389, 33–39.

Kerp, H., 1996. Post-variscan late palaeozoic northern hemisphere gymnosperms: the onset of the mesozoic. Review of Palaeobotany and Palynology 90, 263–285.

Killops, S. D., Killops, V. J., 1993. An introduction to organic geochemistry. Longman Scientific.

King, J. F., de Mayo, P., 1964. Molecular Rearrangements, volume 2, chapter Terpenoid rearrangements. Interscience, 771–840.

Kruge, M. A., 2000. Determination of thermal maturity and organic matter type by principal component analysis of the distributions of polycyclic aromatic compounds. International Journal of Coal Geology 43, 27–51.

Kruge, M. A., Stankiewicz, B. A., Crelling, J. C., Montanari, A., Bensley, D. F., 1994. Fossil charcoal in Cretaceous-Teritary boundary : Evidence of catastrophic firestorm and megawave. Geochimica et Cosmochimica Acta 58, 1393–1397.

Langford, F. F., Blanc-Valleron, M.-M., 1990. Interpreting Rock-Eval Pyrolysis Data Using Graphs of Pyrolizable Hydrocarbons vs. Total Organic Carbon. The American Association of Petroleum Geologist Bulletin 74, 799–804.

Larter, S. R., Bowler, B. F., Li, M., Chen, M., Brincat, D., Bennett, B., Noke, K., Donohoe, P., Simmons, D., Kohnen, M., Allan, J., Telnæs, N., Horstad, I., 1996. Molecular indicators of secondary oil migration distances. Nature 383, 593–597.

Li, M., Larter, S. R., Frolov, Y. B., Bjoroy, M., 1994. Adsorptive Interaction between Nitrogen Compounds and Organic and/or Mineral Phases in Subsurface Rocks. Journal of High Resolution Chromatography 19, 230–236.

Li, M., Larter, S. R., Stoddart, D., Bjorøy, M., 1995. The Geochemistry of Reservoirs, volume 86, chapter Fractionation of pyrrolic nitrogen compounds in petroleum during migration: derivation of migration-related geochemical parameters. Geological Society Special Publication, 103–123.

Li, M., Yao, H., Stasiuk, L. D., Fowler, M. G., Larter, S. R., 1997. Effect of maturity and petroleum expulsion on pyrrolic nitrogen compound yields and distributions in Duvernay Formation petroleum source rocks in central Alberta, Canada. Organic Geochemistry 26, 731–744.

Littke, R., 1993. Deposition, Diagenesis and Weathering of Organic Matter-Rich Sediments, volume 47 of *Lecture Notes in Earth Sciences*. Springer, Berlin.

Littke, R., Leythaeuser, D., Radke, M., Schaefer, R. G., 1990. Petroleum generation and migration in coal seams of the Carboniferous Ruhr Basin, northwest Germany. Organic Geochemistry 16, 247–258.

Lopes, J. A. D., Neto, E. V. S., Mello, M. R., Koike, L., Marsaioli, A. J., de A. M. Reis, F., 1999. 3-Alkyl and 3-carboxyalkyl steranes in marine evaporitic oils of the Potiguar Basin, Brazil. Chemical Geology 158, 1–20.

Lucach, S. O., Bowler, B. F. J., Frewin, N., Larter, S. R., 2002. Variation in alkylphenol distributions in a homogenous oil suite from the Dhahaban petroleum system of Oman. Organic Geochemistry 33, 581–594.

Lutz, R., Gieren, B., Lückge, A., H.Wilkes, R.Littke, 2000. Composition of organic matter in subducted and unsubducted sediments of the Nicoya peninsula, Costa Rica (ODP Leg 170, Sites 1039 and 1040). Organic Geochemistry 31, 1597–1610.

Mackenzie, A. S., Wolff, G. A., Maxwell, J. R., 1983. Fatty Acids in some Biodegraded Petroleums. Possible Origins and Significance. John Wiley & Sons Limited.

Manby, G. M., Lyberis, N., 1996. State of stress and tectonic evolution of the West Spitsbergen Fold Belt. Tectonophysics 267, 1–29.

Martin, W., Gierl, A., Saedler, H., 1989. Molecular evidence for pre-cretaceous angiosperm origins. Nature 339, 46–48.

Marynowski, L., Czechowski, F., Simoneit, D. R. T., 2001. Phenylnaphthalenes and polyphenyls in Paleozoic source rocks of the Holy Cross Mountains, Poland. Organic Geochemistry 32, 69–85.

Masuda, K., Shiojima, K., Ageta, H., 1983. Fern constituents: six tetracyclic triterpenoid hydrocarbons having different carbon skeletons, isolated from *lemmaphyllum microphyllum var. obovatum*. Chem. Pharm. Bull. 31, 2530–2533.

Matsumoto, G. I., Machihara, T., Suzuki, N., Funaki, M., Watanki, K., 1987. Steranes and triterpanes in the Beacon Supergroup samples from southern Victoria Land in Antarctica. Geochimica et Cosmochimca Acta 51, 2668–2671.

Mejanelle, P., Bleton, J., Goursaud, S., Tchapla, A., 1997. Identification of phenolic acids and inositols in balms and tissues from an Egyptian mummy. Journal of Chromatography A 767, 177–186.

Meredith, W., Kelland, S.-J., Jones, D. M., 2000. Influence of biodegradation on crude oil acidity and carboxylic acid composition. Organic Geochemistry 31, 1059–1073.

Meyer zu Reckendorf, R., 1997. Identification of phenyl-substituted polycyclic aromatic compounds in ring furnance gases using GC-MS and GC-AED. Chromatographia 45, 173–182.

Mills, D. A. C., 1982. Geological notes and local details for 1:100,00 shets NZ15NW, NE, SW and SE (Chopwell, Rowlands Gill, Consett and Stanley). BGS Report WA/DM/82/54, Institute of Geological Sciences, Geological Survey of England and Wales.

Mojelsky, T. W., Strausz, O. P., 1986. Detection of alkylated fluorenes in Athabasca oil sand bitumens. Organic Geochemistry 9, 39–45.

Moldowan, J. M., Dahl, J., Huizinga, B. J., Fago, F. J., Hickey, L. J., Peakman, T. M., Taylor, D. W., 1994. The molecular fossil record of oleanane and its relation to angiosperms. Science 265, 768–771.

Moldowan, J. M., Talyzina, N. M., 1998. Biogeochemical Evidence for Dinoflagellate Ancestors in the Early Cambrian. Science 281, 1168–1170.

Moore, P. D., 1989. Peat and Coal: Origin, Facies, and Depositional Models, volume 12, chapter The ecology of peat-forming processes: a review. Elsevier, Amsterdam, 89–103.

Murayama, M., Yamamoto, K., Mimura, K., 1999. Depositional environment of sedimentary rocks inferred from normal fatty acid compositions. Sedimentary Geology 125, 61–68.

Nikishin, A. M., Ziegler, P. A., Stephenson, R. A., Cloetingh, S. A. P. L., Furne, A. V., Fokin, P. A., Ershov, A. V., Bolotov, S. N., Korotaev, M. V., Alekseev,

A. S., Gorbachev, V. I., Shipilov, E. V., Lankreijer, A., Bembinova, E. Y., Shalimov, I. V., 1996. Late Precambrian to Triassic history of the East European Craton: dynamics of sedimentary basin evolution. Tectonophysics 268, 23–63.

Niklas, K. J., Pratt, L. M., 1980. Evidence of Lignin-like Constituents in Early Silurian (Llandoverian) Plant Fossils. Science 209, 396–397.

Norgate, C. M., Boreham, C. J., Wilkens, A. J., 1999. Changes in hydrocarbon maturity indices with coal rank and type, Buller Coalfield, New Zealand. Organic Geochemistry 30, 985–1010.

Oldenburg, T. B. P., Wilkes, H., Horsfield, B., van Duin, A. C. T., Stoddart, D., Wilhelms, A., 2002. Xanthones-novel aromatic oxygen-containing compounds in crude oils. Organic Geochemistry 33, 595–609.

Orr, W. L., Sinninghe Damsté, J. S., 1990. Geochemistry of Sulfur in Fossil Fuels, chapter Geochemistry of sulfur in petroleum systems. ACS Symposium Series 429, 1–29.

Otto, A., Wilde, V., 2001. The Botanical Review, volume 67, chapter Sesqui-, Di-, and Triterpenoids as Chemosystematic Markers in Extant Conifers-A Review. New York Botanical Garden Press, New York, 141–238.

Ourisson, G., Albrecht, P., Rohmer, M., 1979. The hopanoids, paleochemistry and biochemistry of a group of natural products. Pure Applied Chemistry 51, 709–729.

Ourisson, G., Rohmer, M., Poralla, K., 1987. Prokaryotic hopanoids and other polyterpenoid sterol surrogates. Annual Review of Microbiology 41, 301–333.

Peng, P., Morales-Izquierdo, A., Fu, J., Sheng, G., Jiang, J., Hogg, A., Strausz, O. P., 1998. Lanostane sulfides in an immature crude oil. Organic Geochemistry 28, 125–134.

Pentegova, V. A., Dubovenko, Z. V., Vol'skii, L. N., Vasilyuk, S. M., Chirkova, M. A., Shmidt, É. N., 1968. Sesquiterpenoid hydrocarbons from the oleoresins of some siberian conifer species. Siberian Chemistry Journal , 211–214.

Peres, V., Nagem, T. J., 1997. Trioxygenated naturally occurring xanthones. Phytochemistry 44, 191–214.

Peters, K. E., 1986. Guidelines for Evaluating Petroleum Source Rock Using Programmed Pyrolysis. The American Association of Petroleum Geologists Bulletin 70, 318–326.

Peters, K. E., Moldowan, J. M., 1991. Effects of source, thermal maturity, and biodegradation on the distribution and isomerisation of homohopanes in petroleum. Organic Geochemistry 17, 47–61.

Peters, K. E., Moldowan, J. M., 1993. The biomarker guide: interpreting molecular fossils in petroleum and ancient sediments. Prentice Hall, New Jersey.

Piasecki, S., Stemmerik, L., 1991. Modern and Ancient Continental Shelf Anoxia , volume 58, chapter Late Permian anoxia in central East Greenland. Geological Society, 275–290.

Pothuluri, J. V., Freemann, J. P., Evans, F. E., Cerniglia, C. E., 1993. Biotransformation of fluorene by the fungus *Cunninghamella elegans*. Applied and Environmental Microbiology 59, 1977–1980.

Pryer, K. M., Schneider, H., Smith, A. R., Cranfill, R., Wolf, P. G., Hunt, J. S., Sipes, S. D., 2001. Horsetails and ferns are a monophyletic group and the closest living relatives to seed plants. Nature 409, 618–622.

Püttmann, W., Villar, H., 1987. Occurrence and geochemical significance of 1,2,5,6-tetramethylnaphthalene. Geochimica et Cosmochimica Acta 51, 3023–3029.

Qiu, Y.-L., Cho, Y., Cox, J. C., Palmer, J. D., 1998. The gain of three mitochondrial introns identifies liverworts as the earliest land plants. Nature 394, 671–674.

Radke, M., Garrigues, P., Willsch, H., 1990. Methylated dicyclic and tricyclic aromatic hydrocarbons in crude oils from the Handil field, Indonesia. Organic Geochemistry 15, 17–34.

Radke, M., Rullkötter, J., Vriend, S. P., 1994. Distribution of naphthalenes in crude oils from the Java Sea: Source and maturation effects. Geochimica et Cosmochimica Acta 58, 3675–3689.

Radke, M., Schaeffer, R. G., Leythaeuser, D., Teichmüller, M., 1980. Composition of soluble organic matter in coals: relation to rank and liptinite fluorescence. Geochimica et Cosmochimica Acta 44, 1787–1800.

Radke, M., Sittard, H., Welte, H. D., 1978. Removal of soluble organic matter from source rock samples with a flow through extraction cell. Analytical Chemistry 50, 663–665.

Radke, M., Vriend, S. P., Ramanampisoa, L. R., 2000. Alkyldibenzofurans in terrestrial rocks: Influence of organic facies and maturation. Geochimica et Cosmochimica 64, 275–286.

Radke, M., Welte, D. H., Willsch, H., 1982a. Geochemical study on a well in the Western Canada Basin: relation on the aromatic distribution pattern to maturity of organic matter. Geochimica et Cosmochimica Acta 46, 1–10.

Radke, M., Welte, D. H., Willsch, H., 1986. Maturity parameters based on aromatic hydrocarbons: Influence of the organic matter type. Organic Geochemistry 10, 51–63.

Radke, M., Welte, D. H., Willsch, H., 1991. Distribution of alkylated aromatic hydrocarbons and dibenzothiophenes in rocks of the Upper Rhine Graben. Chemical Geology 93, 325–341.

Radke, M., Willsch, H., 1994. Extractable alkyldibenzothiophenes in Posidonia Shale (Toarcian) source rocks: Relationship of yields to petroleum formation and expulsion. Geochimica et Cosmochimica Acta 23, 5223–5244.

Radke, M., Willsch, H., Leythaeuser, D., Teichmüller, M., 1982b. Aromatic components of coal: relation of distribution pattern to rank. Geochimica et Cosmochimica Acta 46, 1831–1848.

Raymond, A., Parker, W. C., Parrish, J. T., 1985. Geological factors and the Evolution of Plants, chapter Phytogeography and Paleoclimate of the Early Carboniferous. Yale Univ. Press, New Haven, CT, 169–222.

Requejo, A. G., 1994. Maturation of petroleum source rocks-II. Quantitative changes in extractable hydrocarbon content and composition associated with hydrocarbon generation. Organic Geochemistry 21, 91–105.

Ribereau-Gayon, P., 1972. Plant Phenolics. Oliver and Boyd, Great Britian.

Richnow, H. H., Annweiler, E., Koning, M., Lüth, J.-C., Stegman, R., Garms, C., Francke, W., Michaelis, W., 2000. Tracing the transformation of labelled [1-^{13}C]phenanthrene in a soil bioreactor. Environmental Pollution 108, 91–101.

Rohmer, M., Bisseret, P., Neunlist, S., 1992. Biological Markers in Sediments and Petroleum, chapter The hopanoids, prokaryotic triterpenoids and precursors of ubiquitous molecular fossils. Prentice-Hall, Englewood Cliffs, NJ, 1–17.

Ross, G. M., 1999. Paleogeography: an earth systems perspective. Chemical Geology 161, 5–16.

Rothman, D. H., 2001. Global biodiversity and the ancient carbon cycle. PNAS 98, 4305–4310.

Rowland, S. J., Alexander, R., Kagi, R. I., 1984. Analysis of trimethylnaphthalenes in petroleum by capillary gas chromatography. Journal of Chromatography 294, 407–412.

Rubinstein, I., Sieskind, O., Albrecht, P., 1975. Rearranged Sterenes in a Shale: Occurrence and Simulated Formation. J. Chem. Soc., Perkin Trans. I, 1833–1836.

Sabaté, J., Grifoll, M., Vinas, M., Solanas, A. M., 1999. Isolation and characterization of a 2-methylphenanthrene utilizing bacterium: identification of ring cleavage metabolites. Applied Microbial Biotechnology 52, 704–712.

Salmon, V., Derenne, S., Lallier-Verges, E., Largeau, C., Beaudoin, B., 2000. Protection of organic matter by mineral matrix in a Cenomanian black shale. Organic Geochemistry 31, 463–474.

Salmon, V., Derenne, S., Largeau, C., Beaudoin, B., Bardoux, G., Mariotti, A., 1997. Kerogen chemical structure and source organisms in a Cenomanian organic-rich black shale (Central Italy)- Indications for an important role of the "sorptive protection" pathway. Organic Geochemistry 27, 423–438.

Schmidt, M., Schneider-Poetsch, H. A. W., 2002. The evolution of gymnosperms redrawn by phytochrome genes: The gnetatae appear at the base of the gymnosperms. Journal of Molecular Evolution 54, 715–724.

Schmitter, J. M., Arpino, P. J., Guiochon, G., 1981. Isolation of degraded pentacyclic triterpenoid acids in a Nigerian crude oil and their identification as tetracyclic carboxylic acids resulting from ring A cleavage. Geochimica et Cosmochimica Acta 45, 1951–1955.

Scotese, C. R., 2000. Paleogeographic atlas. www.scotese.com .

Scotese, C. R., Boucot, A. J., Mckerrow, W. S., 1999. Gondwanan palaeogeography and palaeoclimatology. Journal of African Earth Sciences 28, 99–114.

Scott, A. C., Galtier, J., 1996. A review of the problems in stratigraphical, palaeoecological and palaeobiogeographical interpretation of Lower Carboniferous (Dinantian) floras from Western Europe. Review of Palaeobotany and Palynology 90, 141–153.

Seifert, W. K., 1975. Carboxylic acids in petroleum and sediments. Fortschritte der Chemie organischer Naturstoffe 32, 1–49.

Seifert, W. K., Moldowan, J. M., 1979. The effect of biodegradation on steranes and terpanes in crude oils. Geochimica et Cosmochimica 43, 111–126.

Sephton, M. A., Looy, C. V., Veefkind, R. J., Visscher, H., Brinkhuis, H., de Leeuw, J. W., 1999. Cyclic diaryl ethers in a Late Permian sediment. Organic Geochemistry 30, 267–273.

Sieskind, O., Joly, G., Albrecht, P., 1979. Simulation of the geochemical transformations of sterols: superacid effect of clay minerals. Geochimica et Cosmochimica Acta 43, 1675–1679.

Simoneit, B. R. T., 1986. Biological markers in the sedimentary record, chapter Cyclic terpenoids of the geosphere. Elsevier, Amsterdam, 43–99.

Simoneit, B. R. T., Grimalt, J. O., Wang, T. G., Cox, R. E., Hatcher, P. G., Nissenbaum, A., 1986. Cyclic terpenoids of contemporary resinous plant detritus and of fossil woods, ambers and coals. Organic Geochemistry 10, 877–889.

Sinninghe Damsté, J. S., de Leeuw, J. W., 1990. Analysis, structure and geochemical significance of organically-bound sulphur in the geosphere: State of the art and future research. Organic Geochemistry 16, 1077–1101.

Sinninghe Damsté, J. S., van Duin, A. C. T., Hollander, D., Kohnen, M. E. L., de Leeuw, J. W., 1995. Early diagenesis of bacteriohopanepolyol derivatives: Formation of fossil homohopanoid. Geochimica et Cosmochimica Acta 59, 5141–5147.

Snyder, L. R., 1965. Distribution of Benzocarbazole Isomers in Petroleum as Evidence for their Biogenic Origin. Nature 205, 277.

Stefanova, M., Disnar, J. R., 2000. Composition and early diagenesis of fatty acids in lacustrine sediments, lake Aydat (France). Organic Geochemistry 31, 41–55.

Strachan, M. G., Alexander, R., Kagi, R. I., 1988. Trimethylnaphthalenes in crude oils and sediments: Effects of source and maturity. Geochimica et Cosmochimica Acta 52, 1255–1264.

Strasburger, E., Noll, F., Schenck, H., Schimper, A. F. W., 1991. Lehrbuch der Botanik für Hochschulen. 33 edition. Gustav Fischer Verlag, Stuttgart.

Streibl, M., Herout, V., 1969. Organic Geochemistry, chapter Terpenoids- especially oxygenated mono-, sesqui-, di-, and triterpenes. Springer, 401–424.

Strickberger, M. W., 1996. Evolution, chapter Evolution in Plants and Fungi. 2. edition. Jones and Bartlett Publishers, Sudbury, Massachusetts, USA, 281–306.

Summons, R. E., Jahnke, L. L., 1992. Biological Markers in Sediments and Petroleum, chapter Hopenes and Hopanes Methylated in Ring-A: Correlation of the Hopanoids from Extant Methylotrophic Bacteria with their Fossil Analogues. Prentice-Hall, Englewood Cliffs, N. J., 182–200.

Sun, Y., Wang, G., 2000. A study of the kinetic parameters of individual macerals from Upper Permian coals in South Cina via open-system pyrolysis. International Journal of Coal Geology 44, 293–303.

Takatsu, M., Yamamoto, T., 1993. Analysis of soot from the combustion of alkylbenzenes. Journal of Analytical and Applied Pyrolysis 26, 1993.

Tauber, M., 2000. Analytische Methoden zur Identifizierung von Inhaltsstoffen Baltischen Bernsteins. Ph.D. thesis, Universität Carolo-Wilhelmina Braunschweig.

Taylor, G. H., Teichmüller, M., Davis, A., Diessel, C. F. K., Littke, R., Robert, P., 1998a. Organic Petrology. Gebrüder Borntraeger, Berlin.

Taylor, G. H., Teichmüller, M., Davis, A., Diessel, C. F. K., Littke, R., Robert, P., 1998b. Organic Petrology, chapter The nature of organic matter- macerals and associated minerals. Gebrüder Borntraeger, Berlin, 223.

Taylor, P., Bennettt, B., Jones, M., Larter, S., 2001. The effect of biodegradation and water washing on the occurrence of alkylphenols in crude oils. Organic Geochemistry 32, 341–358.

Taylor, P., Larter, S., Jones, M., Dale, J., Horstad, I., 1997. The effect of oil-water-rock partitioning on the occurrence of alkylphenols in petroleum systems. Geochimica et Cosmochimica Acta 61, 1899–1910.

Taylor, T. N., Hass, H., Remy, W., Kerp, H., 1995. The oldest fossil lichen. Nature 378, 244.

Teichmüller, M., Teichmüller, R., 1968. Coal and Coal-Bearing Strata, chapter Geological aspects of coal metamorphism. Oliver & Boyd, 233–267.

ten Haven, H. L., Littke, R., Rullkötter, J., 1992. Biological Markers in Sediments and Petroleum, chapter Hydrocarbon biological markers in Carboniferous coals of different maturities. Prentice-Hall, Englewood Cliffs, NJ, 142–155.

Thomas, B. A., 1986. Systematic and Taxonomic Approaches in Paleobotany, volume 31 of *Systematic Association Special*, chapter The biochemical analysis of fossil plants and its use in taxonomy and systematics. Clarendon Press, Oxford, 39–51.

Thomas, B. R., 1969. Organic Geochemistry. Methods and results, chapter Kauri resins- modern and fossil. Springer Verlag, Berlin, 599–618.

Thomas, B. R., 1970. Phytochemical Phylogeny, chapter Modern and Fossil Plant Resins. Academic Press, 59–79.

Tissot, B. P., Welte, D. H., 1984. Petroleum Formation and Occurrence. 2 edition. Springer Verlag, Berlin Heidelberg New York Tokyo, 151–159.

Tori, M., Aoki, M., Nakashima, K., Asakawa, Y., 1995. Terpenoids from the liverworts *Symphyogyna Brasiliensis* and unidentified *Frullania* species. Phytochemistry 39, 99–103.

Tritz, J.-P., Herrmann, D., Bisseret, P., Connan, J., Rohmer, M., 1999. Abiotic and biological hopanoid transformation: towards the formation of molecular fossils of the hopane series. Organic Geochemistry 30, 499–514.

Trolio, R., Grice, K., Fisher, S. J., Alexander, R., Kagi, R. I., 1999. Alkylbiphenyls and alkyldiphenylmethanes as indicators of petroleum degradation. Organic Geochemistry 30, 1241–1253.

van Aarssen, B. G. K., Alexander, R., Kagi, R. I., 2001. Applications of aromatic hydrocarbons: The liquid reaction environment in source rocks-a fundamental stage in oil formation. APPEA Journal , 549–558.

van Aarssen, B. G. K., Bastow, T. P., Alexander, R., Kagi, R. I., 1999. Distributions of methylated naphthalenes in crude oils: indicators of maturity, biodegradation and mixing. Organic Geochemistry 30, 1213–1227.

van Aarssen, B. G. K., Cox, H. C., Hoogendoorn, P., de Leeuw, J. W., 1990. A cadinene biopolymer in fossil and extant dammar resins as a source for cadinanes and bicadinanes in crude oils from South East Asia. Geochimica et Cosmochimica Acta 54, 3021–3031.

van Aarssen, B. G. K., Hessels, J. K. C., Abbink, O. A., de Leeuw, J. W., 1992. The occurrence of polycyclic sesqui-, tri- and oligoterpenoids derived from a resinous polymeric cadinene in crude oils from southeast Asia. Geochimica et Cosmochimica Acta 56, 1231–1246.

van Duin, A. C. T., Baas, J. M. A., van de Graaf, B., de Leeuw, J. W., Bastow, T. P., Alexander, R., 1997. Comparison of calculated equilibrium mixtures of alkylnaphthalenes and alkylphenanthrenes with experimental and sedimentary data; the importance of entropy calculations. Organic Geochemstry 26, 275–280.

van Kaam-Peters, H. M. E., Köster, J., van der Gaast, S. J., Dekker, M., de Leeuw, J. W., Sinninghe Damsté, J. S., 1998. The effect of clay minerals on diasterane/sterane ratios. Geochimica et Cosmochimica Acta 62, 2923–2929.

Vickery, J. R., Whitfield, F. B., Ford, G. L., Kennett, B. H., 1984. The fatty acid compositon of gymnospermae seed and leaf oils. Journal of the American Oil Chemists Society 61, 573–575.

Volkman, J. K., Alexander, R., Kagi, R. I., Rowland, S. J., Sheppard, P. N., 1984. Biodegradation of aromatic hydrocarbons in crude oils from the Barrow Sub-basin of Western Australia. Organic Geochemistry 6, 619–632.

Volkman, J. K., Barrett, S. M., Blackburn, S. I., Mansour, M. P., Sikes, E. L., Gelin, F., 1998. Microalgal biomarkers: A review of recent research developments. Organic Geochemistry 29, 1163–1179.

Volkman, J. K., Maxwell, J. R., 1986. Biological markers in the sedimentary record, chapter Acyclic isoprenoids as biological markers. Elsevier, Amsterdam, 1–42.

Wade Jr., L. G., Acker, K. J., Earl, R. A., Osteryoung, R. A., 1979. Cyclodehydration Reactions Using Molten Sodium Tetrachloroaluminate. Journal of Organic Chemistry 44, 1683–1684.

Wantson, J. S., Jones, D. M., Swannell, R. J. P., 1999. In Situ Bioremediation of Petroleum Hydrocarbon and other Organic Compounds, chapter Formation of carboxylic acids during biodegradation of crude oils. Battelle, Columbus, Ohio, 251–255.

White, C. M., Lee, M. L., 1980. Identification and geochemical significance of some aromatic components of coals. Geochimica et Cosmochimica Acta 44, 1825–1832.

Wilhelms, A., Telnæs, N., Steen, A., Augustson, J., 1998. A quantitative study of aromatic hydrocarbons in a natural maturity shale sequence- the 3-methylphenanthrene/retene ratio, a pragmatic maturity parameter. Organic Geochemistry 29, 97–105.

Wilkes, H., Boreham, C., Harms, G., Zengler, K., Rabus, R., 2000. Anaerobic degradation and carbon isotopic fractionation of alkylbenzenes in crude oil by sulphate-reducing bacteria. Organic Geochemistry 31, 101–115.

Wilkes, H., Clegg, H., Disko, U., Willsch, H., Horsfield, B., 1998a. Fluoren-9-ones and carbazoles in the Posidonia Shale, Hils Syncline, northwest Germany. Fuel 7, 657–668.

Wilkes, H., Disko, U., Horsfield, B., 1998b. Aromatic aldehydes and ketones in the Posidonia Shale, Hils Syncline, Germany. Organic Geochemistry 29, 107–117.

Wilkes, H., Ramrath, A., Negendank, J. F. W., 1999. Organic geochemical evidence for environmental changes since 34,000 yrs BP from Lago di Mezzano, central Italy. Journal of Paleolimnology 22, 349–365.

Willsch, H., Clegg, H., Horsfield, B., Radke, M., Wilkes, H., 1997. Liquid chromatographic separation of sediment, rock, and coal extracts and crude oil into compound classes. Analytical Chemistry 69, 4203–4209.

Willsch, H., Radke, M., 1995. Distribution of polycyclic aromatic compounds in coals of high rank. Polycyclic Aromatic Compounds 7, 231–251.

Young, B., Armstrong, M., 1989. The applied geological mapping of the Dearham and Gilcrux area, Cumbria. Technical Report WA/92/70, British Geological Survey.

Young, B., Boland, M. P., 1992. Geology and land-use planning: Great Broughton-Lamplugh area, Cumbria. Technical Report WA/92/54, British Geological Survey.

Zhang, X., Young, L. Y., 1997. Carboxylation as an Initial Reaction in the Anaerobic Metabolism of Naphthalene and Phenanthrene by Sulfidogenic Consortia. Applied and Environmental Microbiology 63, 4759–4764.

Zhong, N. N., Smyth, M., 1997. Striking liptinic bark remains peculiar to some Late Permian Chinese coals. International Journal of Coal Geology 33, 333–349.

Appendix

A Data Compilation

A.1 Bulk Results

Table A.1: Maceral Group Distribution and Data of Elemental Analysis

Sample	Vitrinite	Inertinite	Liptinite	Minerals	TC	TOC	TS
	%	%	%	%	%	%	%
E 49710	94.0	2	4	-	76.8	76.1	1.50
E 49748	1.5	1	1.0	82.0	6.7	4.4	2.05
E 49749	-	-	2.5	97.5	2.7	0.2	1.00
E 49750	0.5	0.5	9.0	86.5	5.3	1.0	1.09
E 49751	0.5	0.5	8.0	89.5	2.5	1.4	1.00
E 48990	83.5	-	16.5	-	80.0	79.4	0.46
E 48478	n.d.	n.d.	n.d.	n.d.	7.1	3.0	0.18
E 48479	0.5	4.0	16.0	79.5	11.5	6.2	0.10
E 48480	32.0	2.0	-	55.1	17.7	16.5	0.16
E 48996	n.d.	n.d.	n.d.	n.d.	68.1	68.2	0.86
E 48388	60.5	13.5	21.5	4.5	71.2	69.1	2.30
E 48389	67.5	5.5	23.0	4.0	78.4	76.1	1.54
E 48390	73.0	10.5	15.5	1.0	78.7	78.7	0.73
E 48214	25.0	57.0	11.0	7.0	75.9	74.5	1.39
E 48216	76.5	10.0	11.0	2.5	75.4	71.2	1.06
E 48403	18.5	2.5	-	79.0	63.7	62.2	7.76
E 48220	73.5	10.5	14.0	1.5	77.5	77.9	0.84
E 48430	76.8	2.8	0.4	20.0	66.3	61.1	1.08
E 48392	n.d.	n.d.	n.d.	n.d.	71.2	70.2	3.70
E 48393	55.0	21.5	21.0	2.5	76.7	75.1	0.96
E 48394	51.0	25.5	14.5	9.0	74.5	73.0	2.40
E 48395	56.0	-	-	44.0	68.5	62.8	7.64
E 48396	49.0	30.0	16.5	4.5	68.7	66.8	1.79
E 48397	53.5	28.5	13.5	4.5	77.7	75.9	3.38
E 48398	63.0	18.0	13.0	6.0	64.4	64.1	9.70
E 48400	64.0	13.5	12.5	10.0	72.5	71.3	2.35
E 48401	39.0	2.5	15.0	43.5	72.9	71.8	1.19
E 48405	n.d.	n.d.	n.d.	n.d.	58.3	25.2	8.75
E 48425	91.2	-	-	8.8	80.7	77.9	0.94
E 48382	19.5	8.5	29.5	42.5	12.4	12.0	4.56
E 48383	61.0	2.0	26.0	11.0	70.6	66.9	2.26
E 48384	16.5	23.5	23.5	20.5	26.3	29.4	0.59
E 48985	-	2.5	61.5	36.0	66.2	66.2	4.50
E 48986	2.0	5.0	60.5	22.5	69.8	68.4	3.86
E 48987	1.5	2.5	61.5	34.5	70.6	69.7	3.71
E 48988	28.0	17.5	29.5	25.0	51.4	50.8	3.51
E 48989	66.5	10.0	14.0	9.5	55.5	54.6	2.65
E 48993	65.5	19.0	13.0	2.5	61.5	58.1	0.81
E 48991	37.0	28.0	31.0	4.0	81.7	81.5	0.47
E 48992	22.0	-	77.0	1.0	66.5	67.2	0.40

n.d.:not determined

Table A.2: Data of Rock-Eval Pyrolysis

Sample	S1	S2	S3	Tmax	PI	HI	OI
	$\frac{mg}{g}$	$\frac{mg}{g}$	$\frac{mg}{g}$	°C	%	$\frac{mgHC}{gTOC}$	$\frac{mg\mathrm{CO_2}}{gTOC}$
E 49710	6.84	237.37	6.29	440	0.03	312	8
E 49748	0.28	12.11	2.36	422	0.02	273	53
E 49749	0.01	0.07	0.24	481	0.12	32	109
E 49750	0.12	1.64	0.37	424	0.70	160	36
E 49751	0.73	4.34	0.21	431	0.14	301	14
E 48990	16.53	208.82	5.40	438	0.07	256	7
E 48478	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48479	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48480	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48996	2.67	184.65	7.84	421	0.20	271	12
E 48388	6.10	177.43	5.44	435	0.03	257	8
E 48389	4.32	156.41	5.54	437	0.03	206	7
E 48390	7.76	201.12	6.07	435	0.04	256	8
E 48214	6.18	189.77	5.93	432	0.03	255	8
E 48216	6.71	200.01	5.28	431	0.03	281	7
E 48403	1.47	71.25	5.06	456	0.02	115	8
E 48220	7.17	190.64	4.98	393	0.04	260	7
E 48430	2.43	58.06	6.17	443	0.04	71	23
E 48392	6.21	180.05	5.47	432	0.03	257	8
E 48393	5.58	227.6	5.44	433	0.02	303	7
E 48394	8.27	203.86	5.58	434	0.04	279	8
E 48395	10.56	158.72	5.20	435	0.06	253	8
E 48396	10.66	222.81	4.05	433	0.05	334	6
E 48397	12.49	271.61	4.35	435	0.04	358	6
E 48398	4.56	179.79	3.94	434	0.02	280	6
E 48400	5.72	205.87	5.26	438	0.03	289	7
E 48401	12.83	172.47	5.66	438	0.07	240	8
E 48405	5.40	122.25	3.05	457	0.04	213	5
E 48425	6.32	40.22	4.03	494	0.14	52	5
E 48382	0.81	10.49	0.49	436	0.07	87	4
E 48383	9.54	154.83	5.10	436	0.06	231	8
E 48384	3.63	52.25	2.24	437	0.06	178	8
E 48985	7.72	457.07	12.88	437	0.02	690	19
E 48986	9.74	392.95	12.46	436	0.03	574	18
E 48987	5.23	489.78	12.62	437	0.01	703	18
E 48988	6.17	131.16	18.95	416	0.05	258	37
E 48989	4.74	81.98	24.14	412	0.06	150	44
E 48993	0.57	88.78	10.27	430	0.01	153	18
E 48991	16.53	208.82	5.40	438	0.07	256	7
E 48992	19.80	333.25	3.41	440	0.06	496	5

n.d.:not determined

Table A.3: Compound Class Distribution of Extractable Organic Matter

Sample	Aliphatic hydrocarbons %	Aromatic hydrocarbons %	NSO-compounds %
E 48478	37.0	10.0	53.1
E 48479	20.8	11.1	68.1
E 48480	7.3	21.3	71.4
E 48388	2.7	29.3	68.0
E 48389	2.3	27.0	70.7
E 48390	2.4	24.3	73.4
E 48214	1.7	29.5	68.8
E 48216	1.9	23.2	74.8
E 48430	5.0	0.5	90.0
E 48403	10.8	41.4	47.9
E 48220	3.4	34.7	61.9
E 48392	2.0	23.5	74.6
E 48393	2.3	20.7	77.0
E 48394	1.9	21.3	76.8
E 48395	4.7	19.4	75.9
E 48396	5.7	24.2	70.1
E 48397	10.9	15.8	73.3
E 48398	4.1	22.1	73.8
E 48400	4.1	27.2	68.7
E 48401	2.3	14.7	83.0
E 48405	0.9	34.2	64.9
E 48382	2.5	33.5	64.0
E 48383	3.8	33.1	63.1
E 48384	9.9	28.3	61.8

A.2 Aliphatic Hydrocarbons

For samples where no standard was added, the concentrations of all compounds are normalised to the compound showing highest amounts (100%)

Table A.4: Nomenclature of n-Alkanes

Compound	Abbreviation
Dodecane	n-C_{12}
Tridecane	n-C_{13}
Tetradecane	n-C_{14}
Pentadecane	n-C_{15}
Hexadecane	n-C_{16}
Heptadecane	n-C_{17}
Octadecane	n-C_{18}
Nonadecane	n-C_{19}
Eicosane	n-C_{20}
Heneicosane	n-C_{21}
Docosane	n-C_{22}
Tricosane	n-C_{23}
Tetracosane	n-C_{24}
Pentacosane	n-C_{25}
Hexacosane	n-C_{26}
Heptacosane	n-C_{27}
Octacosane	n-C_{28}
Nonacosane	n-C_{29}
Triacontane	n-C_{30}
Hentricontane	n-C_{31}
Dotricontane	n-C_{32}
Tritricontane	n-C_{33}
Tetratricontane	n-C_{34}

Table A.5: Concentrations of *n*-Alkanes

Sample	*n*-C_{12} $\frac{\mu g}{gTOC}$	*n*-C_{13} $\frac{\mu g}{gTOC}$	*n*-C_{14} $\frac{\mu g}{gTOC}$	*n*-C_{15} $\frac{\mu g}{gTOC}$	*n*-C_{16} $\frac{\mu g}{gTOC}$	*n*-C_{17} $\frac{\mu g}{gTOC}$
E 49710	0.89	6.25	9.67	15.31	16.61	19.34
E 48990	0.01	0.08	0.34	0.72	1.11	1.24
E 48996	0.18	0.53	0.29	1.50	3.22	5.87
E 48388	0.03	0.62	0.13	0.92	4.64	11.56
E 48389	4.35	8.66	12.25	13.94	14.18	16.30
E 48390	9.24	15.58	20.02	23.01	23.91	27.06
E 48214	17.33	24.43	30.19	30.50	30.73	31.85
E 48216	8.87	14.65	23.31	23.26	23.66	24.82
E 48403	0.06	0.63	2.90	8.12	15.21	21.38
E 48220	1.62	5.92	12.90	17.09	20.19	24.49
E 48392	n.d.	n.d.	n.d.	n.d.	n.d	n.d.
E 48393	1.29	3.26	5.10	6.03	6.08	7.04
E 48394	2.97	5.25	6.70	7.65	7.93	9.46
E 48395	3.46	0.42	0.78	1.28	6.10	41.81
E 48396	1.45	4.47	8.31	11.45	12.68	14.40
E 48397	1.00	4.33	10.31	17.74	24.31	31.66
E 48398	0.47	1.56	3.12	4.69	6.14	7.46
E 48400	0.57	1.77	3.56	5.97	7.59	9.51
E 48401	1.00	3.49	6.59	9.17	11.41	13.46
E 48405	0.84	4.80	10.67	14.75	16.42	16.81
E 48382	0.13	0.60	3.16	7.14	9.65	12.25
E 48383	1.69	6.40	11.50	17.29	19.85	30.33
E 48384	5.54	15.18	24.83	33.61	39.42	47.39
E 48985	0.10	0.79	6.01	3.02	17.81	64.28
E 48986	0.04	0.18	0.81	3.24	9.11	18.94
E 48987	0.03	0.22	0.53	1.93	3.80	8.45
E 48988	0.25	1.22	2.44	2.73	5.73	33.52
E 48989	0.15	0.98	1.65	5.97	11.07	16.17
E 48993	0.02	0.63	0.50	2.02	3.05	5.43
E 48991	0.02	0.06	0.34	1.81	4.97	8.47
E 48992	0.02	0.37	4.77	18.55	36.70	51.52

n.d.:not detected

Table A.5: (continued)

Sample	n-C_{18} $\frac{\mu g}{gTOC}$	n-C_{19} $\frac{\mu g}{gTOC}$	n-C_{20} $\frac{\mu g}{gTOC}$	n-C_{21} $\frac{\mu g}{gTOC}$	n-C_{22} $\frac{\mu g}{gTOC}$	n-C_{23} $\frac{\mu g}{gTOC}$
E 49710	14.87	18.54	15.36	18.10	21.12	28.41
E 48990	1.20	1.05	2.81	0.82	0.78	0.74
E 48996	5.00	6.93	7.34	10.03	14.54	35.46
E 48388	19.74	28.13	28.93	32.08	29.79	31.34
E 48389	16.83	19.66	18.99	21.11	19.42	20.18
E 48390	27.01	30.26	29.85	31.05	27.92	28.33
E 48214	32.94	36.21	31.09	34.13	28.33	28.72
E 48216	27.06	30.67	27.54	32.61	26.43	27.95
E 48403	28.06	31.27	34.59	36.66	37.12	36.28
E 48220	23.85	27.54	23.22	26.52	21.33	21.33
E 48392	n.d.	n.d.	n.d.	n.d.	n.d	n.d.
E 48393	6.97	7.02	6.27	6.61	6.52	7.11
E 48394	9.48	11.00	10.91	11.99	12.36	13.01
E 48395	71.43	144.73	59.52	32.89	13.44	8.22
E 48396	14.18	16.29	16.51	18.37	17.11	18.20
E 48397	34.74	40.67	41.77	45.40	44.99	47.28
E 48398	8.37	9.06	8.89	9.91	9.59	10.36
E 48400	10.87	13.52	13.90	16.52	15.89	17.49
E 48401	14.08	16.24	14.81	16.91	15.29	16.30
E 48405	15.82	12.82	10.18	7.70	6.26	4.58
E 48382	13.21	15.63	16.60	18.65	20.21	21.89
E 48383	27.89	32.61	33.99	37.60	37.68	40.50
E 48384	48.77	56.28	57.55	60.16	51.09	47.70
E 48985	77.45	85.07	88.53	276.20	335.93	446.25
E 48986	20.35	18.99	20.01	18.56	18.74	26.67
E 48987	10.95	16.36	28.13	49.10	53.06	40.60
E 48988	49.44	49.74	40.73	26.11	22.22	19.19
E 48989	17.02	7.34	12.75	17.11	19.84	28.52
E 48993	8.08	18.83	29.40	57.10	116.60	274.47
E 48991	10.25	12.38	17.33	21.00	29.49	40.91
E 48992	56.95	62.35	71.55	89.89	93.03	108.57

n.d.:not detected

Table A.5: (continued)

Sample	*n*-C_{24} $\frac{\mu g}{gTOC}$	*n*-C_{25} $\frac{\mu g}{gTOC}$	*n*-C_{26} $\frac{\mu g}{gTOC}$	*n*-C_{27} $\frac{\mu g}{gTOC}$	*n*-C_{28} $\frac{\mu g}{gTOC}$	*n*-C_{29} $\frac{\mu g}{gTOC}$
E 49710	32.38	38.37	36.30	40.17	30.92	31.80
E 48990	0.83	0.96	1.02	1.15	1.07	1.01
E 48996	57.45	100.83	98.34	174.61	110.55	167.27
E 48388	29.71	30.71	29.97	29.91	26.50	28.08
E 48389	19.10	19.08	17.51	16.50	13.80	13.44
E 48390	26.61	25.18	21.73	19.58	15.33	15.11
E 48214	27.16	26.13	25.94	24.74	21.95	21.57
E 48216	26.93	27.81	27.26	26.83	22.75	23.84
E 48401	33.19	30.63	25.79	22.34	15.64	12.96
E 48220	20.70	20.37	18.94	17.40	15.85	13.63
E 48392	n.d.	n.d.	n.d.	n.d.	n.d	n.d.
E 48393	6.75	7.02	6.94	6.81	5.80	5.54
E 48394	11.36	11.78	10.01	10.40	7.46	7.18
E 48395	4.83	2.97	1.87	1.51	1.30	1.14
E 48396	16.34	17.24	14.59	15.65	12.37	12.62
E 48397	41.80	40.84	33.09	31.58	24.14	22.49
E 48398	9.73	10.20	9.62	9.99	7.84	8.07
E 48400	15.43	17.11	13.35	14.65	10.01	9.77
E 48401	15.28	15.43	14.07	13.85	10.25	10.22
E 48405	3.63	3.05	2.27	1.90	1.58	2.10
E 48382	21.18	21.31	19.92	20.26	17.51	18.62
E 48383	39.09	39.57	37.34	36.42	26.25	26.82
E 48384	39.78	37.18	30.50	27.28	21.47	18.72
E 48985	450.53	591.65	424.52	609.79	296.54	428.60
E 48986	26.52	38.83	34.32	50.44	31.21	38.64
E 48987	25.65	23.54	18.21	28.49	18.39	24.66
E 48988	18.99	16.39	15.23	12.48	12.78	10.18
E 48989	20.34	81.75	40.25	451.02	76.42	1330.81
E 48993	401.33	1156.57	528.01	1419.46	72.46	108.89
E 48991	40.15	37.64	30.33	26.39	14.66	12.93
E 48992	107.31	109.25	99.04	87.93	61.67	46.13

n.d.:not detected

Table A.5: (continued)

Sample	n-C_{30} $\frac{\mu g}{gTOC}$	n-C_{31} $\frac{\mu g}{gTOC}$	n-C_{32} $\frac{\mu g}{gTOC}$	n-C_{33} $\frac{\mu g}{gTOC}$	n-C_{34} $\frac{\mu g}{gTOC}$	n-C_{12}-n-C_{34} $\frac{\mu g}{gTOC}$
E 49710	19.25	16.42	7.30	14.10	6.66	458.13
E 48990	0.89	0.81	0.79	2.07	1.02	22.50
E 48996	72.82	93.82	37.63	42.54	22.40	1069.14
E 48388	18.09	16.73	7.93	11.09	4.82	421.46
E 48389	9.23	9.15	4.34	7.86	4.56	320.43
E 48390	9.46	8.39	5.01	5.75	2.52	447.92
E 48214	13.98	13.10	6.54	7.83	3.91	549.31
E 48216	15.60	16.18	6.60	10.99	3.75	499.37
E 48403	8.67	6.05	3.96	5.68	2.37	419.58
E 48220	9.28	7.69	4.21	6.33	2.59	363.00
E 48392	n.d.	n.d.	n.d.	n.d.	n.d	n.d.
E 48393	3.84	3.17	1.86	2.60	1.20	120.83
E 48394	4.29	4.19	2.12	4.81	4.22	186.53
E 48395	0.57	1.61	0.69	2.11	2.69	405.35
E 48396	9.08	7.51	5.19	7.24	3.54	274.83
E 48397	16.25	12.03	8.07	8.35	5.09	587.93
E 48398	5.23	3.70	2.26	3.66	1.64	151.54
E 48400	6.50	5.33	3.14	6.04	3.15	221.65
E 48401	5.58	4.23	2.11	4.45	4.54	238.74
E 48405	0.89	1.08	0.44	0.62	0.25	139.43
E 48382	13.62	11.11	6.81	6.56	3.47	299.53
E 48383	16.30	14.91	7.60	9.41	3.77	554.80
E 48384	14.00	10.33	7.55	7.07	4.47	705.89
E 48985	209.76	381.06	145.47	164.95	99.69	5203.98
E 48986	25.76	38.59	26.67	86.96	42.53	596.10
E 48987	14.93	33.79	23.59	81.43	37.45	543.28
E 48988	10.59	8.06	7.59	4.35	4.48	374.45
E 48989	81.21	865.32	34.92	111.66	7.27	3239.55
E 48993	19.33	15.65	14.26	32.04	7.40	4291.55
E 48991	7.43	6.26	4.15	5.48	4.58	337.01
E 48992	30.48	22.31	18.67	22.36	12.99	1212.42

n.d.:not detected

Table A.6: Distribution of *n*-Alkanes (samples without standard)

Sample	*n*-C_{12} %	*n*-C_{13} %	*n*-C_{14} %	*n*-C_{15} %	*n*-C_{16} %	*n*-C_{17} %
E 48478	0.0	0.1	2.0	7.1	15.1	25.9
E 48479	0.3	1.8	14.2	38.2	58.0	77.7
E 48480	n.d.	n.d.	17.7	61.2	100.0	87.0
E 49748	5.2	13.8	20.6	28.7	34.1	39.7
E 49749	3.7	7.4	7.0	10.4	13.1	14.9
E 49750	2.9	58.1	70.5	63.9	92.5	100.0
E 49751	0.7	4.9	13.5	23.4	33.1	40.0
E 48430	0.7	5.0	15.1	28.6	35.2	44.3
E 48425	0.3	0.9	3.6	9.7	76.5	27.9

n.d.:not detected

Table A.6: (continued)

Sample	*n*-C_{18} %	*n*-C_{19} %	*n*-C_{20} %	*n*-C_{21} %	*n*-C_{22} %	*n*-C_{23} %
E 48478	39.1	56.8	70.3	100.0	80.4	80.5
E 48479	80.9	92.7	100.0	96.1	90.8	89.8
E 48480	61	n.d.	n.d.	n.d.	n.d.	n.d.
E 49748	33.2	33.7	31.1	29.2	30.7	32.2
E 49749	17.0	21.6	26.1	26.8	31.9	40.7
E 49750	91.2	90.0	80.8	67.2	62.9	57.7
E 49751	41.1	45.3	49.4	43.7	46.3	44.2
E 48430	47.5	64.5	60.8	63.2	53.9	57.6
E 48425	21.5	25.1	32.7	45.3	55.1	73.2

n.d.:not detected

Table A.6: (continued)

Sample	*n*-C_{24} %	*n*-C_{25} %	*n*-C_{26} %	*n*-C_{27} %	*n*-C_{28} %	*n*-C_{29} %
E 48478	78.1	76.8	71.4	65.6	59.8	51.4
E 48479	73.4	68.4	52.9	48.1	38.8	38.1
E 48480	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 49748	32.1	32.3	30.1	34.5	29.9	36.5
E 49749	50.5	63.4	63.9	84.7	65.6	100.0
E 49750	48.5	43.0	34.6	34.6	29.0	30.8
E 49751	42.9	40.9	39.0	43.8	44.7	48.6
E 48430	53.7	60.5	47.4	53.2	31.0	29.2
E 48425	73.9	97.0	69.6	100.0	48.6	70.3

n.d.:not detected

Table A.6: (continued)

Sample	*n*-C_{30} %	*n*-C_{31} %	*n*-C_{32} %	*n*-C_{33} %	*n*-C_{34} %
E 48478	35.0	29.0	15.9	23.9	9.8
E 48479	27.5	25.6	17.7	14.6	10.1
E 48480	n.d.	n.d.	n.d.	n.d.	n.d.
E 49748	25.6	29.1	18.4	30.7	20.5
E 49749	54.9	69.0	36.8	64.4	30.8
E 49750	26.2	28.5	20.4	24.6	16.1
E 49751	42.8	40.5	30.5	43.3	38.7
E 48430	14.7	16.3	6.5	13.6	3.3
E 48425	34.4	62.5	23.9	27.1	16.4

n.d.:not detected

Table A.7: Concentrations of Pristane and Phytane

Sample	Pristane $\frac{\mu g}{gTOC}$	Phytane $\frac{\mu g}{gTOC}$
E 49710	65.85	9.67
E 48990	1.38	0.47
E 48996	32.63	9.8
E 48388	42.73	12.25
E 48389	46.98	10.17
E 48390	71.72	13.27
E 48214	68.65	13.54
E 48216	117.34	22.05
E 48403	29.19	8.49
E 48220	67.94	13.37
E 48392	n.d.	n.d.
E 48393	21.03	4.73
E 48394	41.97	8.57
E 48395	9.97	7.88
E 48396	46.95	10.76
E 48397	20.92	7.24
E 48398	18.36	4.99
E 48400	26.28	6.08
E 48401	30.74	6.37
E 48405	7.69	3.28
E 48382	44.72	7.98
E 48383	171.70	31.75
E 48384	8.03	3.54
E 48985	47.51	96.98
E 48986	7.04	7.22
E 48987	1.38	1.68
E 48988	28.12	47.27
E 48989	7.24	8.95
E 48993	7.01	2.29
E 48991	5.31	1.57
E 48992	40.96	8.62

n.d.:not detected

Table A.8: Distribution of Pristane and Phytane (samples without standard)

Sample	Pristane %	Phytane %
E 48478	17.3	14.2
E 48479	39.2	22.5
E 48480	n.d.	n.d.
E 49748	100.0	77.6
E 49749	21.8	18.8
E 49750	89.2	49.9
E 49751	100.0	59.8
E 48430	100.0	15.9
E 48425	22.6	19.9

n.d.:not detected

Table A.9: Nomenclature of Steranes and Diasteranes

Abbreviation	Name
$S\beta\alpha$DC	(20*S*)-13β(H),17α(H)-Diacholestane
$R\beta\alpha$DC	(20*R*)-13β(H),17α(H)-Diacholestane
$R\alpha\beta$DC	(20*R*)-13α(H),17β(H)-Diacholestane
$S\alpha\beta$DC	(20*S*)-13α(H),17β(H)-Diacholestane
$S\alpha\alpha\alpha$C	(20*S*)-5α(H),14α(H),17α(H)-Cholestane
$R\alpha\beta\beta$C	(20*R*)-5α(H),14β(H),17β(H)-Cholestane
$S\alpha\beta\beta$C	(20*S*)-5α(H),14β(H),17β(H)-Cholestane
$R\alpha\alpha\alpha$C	(20*R*)-5α(H),14α(H),17α(H)-Cholestane
$S\beta\alpha$MDC	(20*S*)-24-Methyl-13β(H),17α(H)-diacholestane
$R\beta\alpha$MDC	(20*R*)-24-Methyl-13β(H),17α(H)-diacholestane
$R\alpha\beta$MDC	(20*R*)-24-Methyl-13α(H),17β(H)-diacholestane
$S\alpha\beta$MDC	(20*S*)-24-Methyl-13α(H),17β(H)-diacholestane
$S\alpha\alpha\alpha$MC	(20*S*)-24-Methyl-5α(H),14α(H),17α(H)-cholestane
$R\alpha\beta\beta$MC	(20*R*)-24-Methyl-5α(H),14β(H),17β(H)-cholestane
$S\alpha\beta\beta$MC	(20*S*)-24-Methyl-5α(H),14β(H),17β(H)-cholestane
$R\alpha\alpha\alpha$MC	(20*R*)-24-Methyl-5α(H),14α(H),17α(H)-cholestane
$S\beta\alpha$EDC	(20*S*)-24-Ethyl-13β(H),17α(H)-diacholestane
$R\beta\alpha$EDC	(20*R*)-24-Ethyl-13β(H),17α(H)-diacholestane
$R\alpha\beta$EDC	(20*R*)-24-Ethyl-13α(H),17β(H)-diacholestane
$S\alpha\beta$EDC	(20*S*)-24-Ethyl-13α(H),17β(H)-diacholestane
$S\alpha\alpha\alpha$EC	(20*S*)-24-Ethyl-5α(H),14α(H),17α(H)-cholestane
$R\alpha\beta\beta$EC	(20*R*)-24-Ethyl-5α(H),14β(H),17β(H)-cholestane
$S\alpha\beta\beta$EC	(20*S*)-24-Ethyl-5α(H),14β(H),17β(H)-cholestane
$R\alpha\alpha\alpha$EC	(20*R*)-24-Ethyl-5α(H),14α(H),17α(H)-cholestane

Table A.10: Distribution of Steranes and Diasteranes

Sample	$S\beta\alpha$DC	$20R\beta\alpha$DC	$R\alpha\beta$DC	$S\alpha\beta$DC	$S\alpha\alpha\alpha$C	$R\alpha\beta\beta$C
	%	%	%	%	%	%
E 48478	0.0	0.0	0.0	0.0	0.0	0.0
E 48479	0.0	0.0	0.0	0.0	0.0	0.0
E 48480	0.0	0.0	0.0	0.0	0.0	0.0
E 48990	5.3	6.9	0.0	0.0	0.0	0.0
E 48996	0.0	0.0	0.0	0.0	0.0	0.0
E 48216	7.2	7.3	0.0	0.0	0.0	0.0
E 48220	41.2	25.7	0.0	19.6	0.0	0.0
E 48430	39.7	31.9	10.2	11.5	17.6	17.3
E 48398	6.6	9.2	2.0	6.2	0.0	0.0
E 48400	14.4	16.9	0.0	0.0	0.0	0.0
E 48401	2.8	4.8	0.0	0.0	0.0	0.0
E 48382	35.6	24.3	0.0	0.0	0.0	0.0
E 48383	0.0	0.0	0.0	0.0	0.0	0.0
E 48384	32.4	32.0	11.9	12.6	0.0	0.0
E 48986	0.0	0.0	0.0	0.0	0.0	0.0
E 48987	0.0	0.0	0.0	0.0	0.0	0.0
E 48988	0.0	0.0	0.0	0.0	0.0	0.0
E 48989	0.0	0.0	0.0	0.0	0.0	0.0
E 48993	3.1	0.0	0.0	0.0	0.0	0.0
E 48992	38.2	13.0	0.0	0.0	0.0	0.0

Table A.10: (continued)

Sample	$S\alpha\beta\beta$C	$R\alpha\alpha\alpha$C	$S\beta\alpha$MDC	$R\beta\alpha$MDC	$R\alpha\beta$MDC	$S\alpha\beta$MDC
	%	%	%	%	%	%
E 48478	0.0	37.7	0.0	0.0	0.0	0.0
E 48479	0.0	6.6	0.0	0.0	0.0	0.0
E 48480	0.0	98.2	0.0	0.0	0.0	0.0
E 48990	0.0	15.0	0.0	0.0	0.0	0.0
E 48996	0.0	45.3	100.0	54.0	0.0	0.0
E 48216	0.0	7.5	18.6	30.0	10.8	0.0
E 48220	0.0	13.2	100.0	72.2	52.8	28.3
E 48430	12.7	1.6	100.0	76.4	28.4	33.6
E 48398	0.0	0.0	81.7	71.5	0.2	1.9
E 48400	0.0	0.0	100.0	69.2	16.4	10.4
E 48401	0.0	0.0	45.6	16.2	0.0	0.0
E 48382	0.0	0.0	82.6	61.1	41.7	0.0
E 48383	0.0	42.4	0.0	0.0	0.0	0.0
E 48384	0.0	50.0	47.5	42.2	24.9	0.0
E 48986	0.0	73.5	0.0	0.0	0.0	0.0
E 48987	0.0	74.2	0.0	0.0	0.0	0.0
E 48988	0.0	73.0	0.0	0.0	0.0	0.0
E 48989	0.0	21.9	0.0	0.0	0.0	0.0
E 48993	0.0	6.6	8.6	7.1	8.2	8.4
E 48992	0.0	53.4	100.0	76.9	17.8	0.0

Table A.10: (continued)

Sample	$S\alpha\alpha\alpha$MC %	$R\alpha\beta\beta$MC %	$S\alpha\beta\beta$MC %	$R\alpha\alpha\alpha$MC %	$S\beta\alpha$EDC %	$R\beta\alpha$EDC %
E 48478	0.0	0.0	0.0	100.0	0.0	0.0
E 48479	0.0	0.0	0.0	100.0	0.0	0.0
E 48480	0.0	0.0	0.0	95.02	0.0	0.0
E 48990	0.0	0.0	0.0	13.9	19.4	45.3
E 48996	0.0	0.0	12.6	95.4	3.3	52.1
E 48216	0.0	0.0	0.0	24.5	100.0	28.7
E 48220	40.3	37.4	32.9	38.2	83.4	78.6
E 48430	8.5	24.7	17.5	2.0	64.2	35.6
E 48398	0.0	0.0	0.0	0.0	6.9	100.0
E 48400	0.0	0.0	0.0	0.0	48.6	54.3
E 48401	0.0	0.0	0.0	100.0	0.0	0.0
E 48382	0.0	0.0	0.0	32.8	100.0	63.3
E 48383	0.0	0.0	0.0	45.3	0.0	0.0
E 48384	0.0	0.0	0.0	21.0	16.5	34.1
E 48986	0.0	0.0	0.0	87.4	0.0	0.0
E 48987	0.0	0.0	0.0	71.1	0.0	0.0
E 48988	0.0	0.0	0.0	100.0	0.0	0.0
E 48989	0.0	0.0	0.0	28.3	0.0	0.0
E 48993	0.0	0.0	10.9	25.1	12.0	12.7
E 48992	0.0	0.0	46.8	86.8	29.9	0.0

Table A.10: (continued)

Sample	*Rαβ*EDC %	*Sαβ*EDC %	*Sααα*EC %	*Rαββ*EC %	*Sαββ* %	EC*Rααα*EC %
E 48478	0.0	0.0	0.0	0.0	0.0	68.5
E 48479	0.0	0.0	0.0	0.0	0.0	12.7
E 48480	0.0	0.0	0.0	0.0	0.0	100.0
E 48990	14.4	11.8	25.8	86.6	86.2	100.0
E 48996	44.3	0.0	20.9	55.0	0.0	54.3
E 48216	22.1	13.6	86.8	65.4	43.7	52.3
E 48220	72.0	64.4	99.1	85.8	67.1	67.0
E 48430	17.7	19.2	48.9	18.8	34.6	46.2
E 48398	54.0	43.1	0.0	0.0	0.0	0.0
E 48400	0.0	0.0	0.0	0.0	0.0	0.0
E 48401	0.0	0.0	0.0	0.0	0.0	0.0
E 48382	0.0	0.0	0.0	0.0	0.0	0.0
E 48383	0.0	0.0	0.0	0.0	0.0	100.0
E 48384	0.0	0.0	0.0	0.0	0.0	100.0
E 48986	0.0	0.0	0.0	0.0	0.0	100.0
E 48987	0.0	0.0	0.0	0.0	0.0	100.0
E 48988	0.0	0.0	0.0	0.0	0.0	98.8
E 48989	0.0	0.0	0.0	0.0	0.0	100.0
E 48993	0.0	0.0	0.0	0.0	42.1	100.0
E 48992	25.7	27.4	8.7	28.1	27.7	64.6

Table A.11: Definition of Sterane- and Diasterane-Ratios

$\frac{20S}{20S+20R} = \frac{20R}{20S+20R}$ of 5α(H),14α(H),17α-C_{29}-Steranes
$\frac{\beta\beta}{\alpha\alpha+\beta\beta} = \frac{2\ (14\beta(H),17\beta(H),20R+S)}{2\ (14\beta(H),17\beta(H),20R+S)+(14\alpha(H),17\alpha(H),20R+S)}$ of C_{29}-steranes
$\frac{C_{29-Diasteranes}}{C_{29-Steranes}} = \frac{13\beta,17\alpha(H),20R+S)-C_{29-Diasteranes}}{5\alpha,14\alpha,17\alpha(H),20R+S)-+(5\alpha,14\beta,17\beta(H)20R+S)-C_{29-Steranes}}$

Table A.12: Ratios of Steranes and Diasteranes

Sample	$\frac{20S}{20S+20R}$	$\frac{\beta\beta}{\alpha\alpha+\beta\beta}$	$\frac{C_{29-Diasteranes}}{C_{29-Steranes}}$
E 48216	0.57	0.61	0.40
E 48220	0.54	0.65	0.26
E 48430	0.72	0.53	0.01
E 48990	0.24	0.73	0.05
E 48992	0.24	0.60	0.67

Table A.13: Nomenclature of Hopanes

Abbreviation	Compound
αTNH	17α(H)-22,29,30-Trinorhopane
βTNH	17β(H)-22,29,30-Trinorhopane
αDNH	17α(H)-28,30-Dinorhopane
$\alpha\beta$NH	17α(H),21β(H)-30-Norhopane
$\beta\alpha$NM	17β(H),21α(H)-30-Normoretane
2MH	2-Methylhopane?
$\alpha\beta$H	17α(H),21β(H)-Hopane
$\beta\beta$NH	17β(H)21β(H)-30-Norhopane
$\beta\alpha$M	17β(H),21α(H)-Moretane
$S\alpha\beta$HH	(22S)-17α(H),21β(H)-29-Homohopane
$R\alpha\beta$HH	(22R)-17α(H),21β(H)-29-Homohopane
S+$R\beta\alpha$HM	(22S)- + (22R)- 17β(H),21α(H)-29-Homomoretane
$\beta\beta$H	17β(H),21β(H)-Hopane
$S\alpha\beta$DHH	(22S)-17α(H),21β(H)-29-Dihomohopane
$R\alpha\beta$DHH	(22R)-17α(H),21β(H)-29-Dihomohopane
S + 22$R\beta\alpha$DHM	(22S)- + (22R)- 17β(H),21α(H)-29-Dihomomoretane
THH	Trihomohopane
THH	Trihomohopane

Table A.14: Concentrations of Hopanes

Sample	αTNH	βTNH	αDNH	α-βNH	$\beta\alpha$NM	2MH
	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$
E 49710	38.90	0.00	3.77	0.00	49.67	9.10
E 48990	0.48	0.04	0.00	0.00	0.36	0.07
E 48996	59.45	0.00	25.71	0.00	33.55	32.22
E 48388	56.77	0.00	0.00	0.00	99.81	8.51
E 48389	28.86	0.00	0.85	0.00	48.87	5.43
E 48390	15.44	0.00	0.34	0.00	16.11	1.44
E 48214	33.68	0.00	0.79	0.00	44.52	5.02
E 48220	35.21	0.00	1.31	0.00	55.31	5.87
E 48393	13.79	0.00	0.43	0.00	21.42	2.08
E 48394	14.28	0.00	0.39	0.00	29.65	2.17
E 48396	13.17	0.00	0.00	0.00	18.22	1.64
E 48397	16.60	0.00	0.26	0.00	6.12	0.74
E 48398	4.70	0.00	0.17	0.00	2.95	0.34
E 48400	10.51	0.00	0.60	0.00	13.99	1.16
E 48401	1.55	0.00	0.00	0.00	1.13	0.11
E 48382	3.85	0.00	0.12	0.00	1.88	0.19
E 48383	39.26	0.00	1.09	0.00	57.54	4.61
E 48384	3.61	0.00	0.00	0.00	0.49	0.00
E 48985	144.42	2.99	405.50	9.16	380.35	203.01
E 48986	4.55	0.18	13.55	0.69	13.53	8.05
E 48987	3.79	0.08	8.42	0.32	8.05	4.76
E 48988	1.85	0.00	0.19	0.00	1.17	0.20
E 48989	2.39	0.00	1.27	0.42	0.55	0.56
E 48993	9.66	0.01	3.54	0.00	9.43	5.35
E 48991	1.87	0.00	0.12	0.00	0.65	0.08
E 48992	26.22	0.22	0.93	0.39	19.64	2.68

Table A.14: (continued)

Sample	$\alpha\beta$H	$\beta\beta$NH	$\beta\alpha$M	$S\alpha\beta$HH	$R\alpha\beta$HH	S+$R\beta\alpha$HM
	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$
E 49710	0.00	58.23	3.15	10.71	39.40	27.47
E 48990	0.00	1.30	0.05	0.00	0.44	0.26
E 48996	11.54	99.77	55.56	13.59	30.71	29.42
E 48388	0.00	56.14	3.46	11.81	27.86	17.30
E 48389	0.00	28.96	2.57	6.14	14.43	10.24
E 48390	0.00	13.49	0.99	2.90	8.38	5.80
E 48214	0.00	21.14	1.95	5.42	12.05	7.50
E 48220	0.00	41.87	4.87	8.50	27.88	17.74
E 48393	0.00	14.17	2.29	2.70	9.24	6.23
E 48394	0.00	18.13	1.99	2.73	13.69	8.16
E 48396	0.00	14.93	1.61	2.87	8.78	5.73
E 48397	0.00	6.76	0.46	1.29	2.82	2.27
E 48398	0.00	2.50	0.53	0.51	1.54	1.19
E 48400	0.00	11.13	0.97	2.15	8.49	5.71
E 48401	0.00	0.86	0.21	0.18	0.41	0.26
E 48382	0.00	1.80	0.20	0.37	0.84	0.63
E 48383	0.00	55.42	1.78	6.89	16.64	11.67
E 48384	0.00	0.47	0.00	0.00	0.00	0.00
E 48985	29.06	295.08	89.10	392.20	30.80	409.50
E 48986	1.45	9.58	2.90	14.20	1.39	12.69
E 48987	0.80	5.76	4.03	9.67	0.41	8.42
E 48988	0.00	1.88	0.59	0.00	0.00	0.00
E 48989	0.00	0.57	0.14	1.58	0.00	0.11
E 48993	0.00	9.45	6.77	1.95	7.03	15.42
E 48991	0.00	1.25	0.00	0.00	0.44	0.22
E 48992	0.00	17.14	11.29	5.32	9.90	6.16

Table A.14: (continued)

Sample	$\beta\beta$H	$S\alpha\beta$DHH	$R\alpha\beta$DHH	$S + 22R\beta\alpha$DHM	THH	THH
	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$
E 49710	9.10	0.00	42.12	29.70	0.00	1.16
E 48990	0.00	0.00	0.18	0.10	0.00	0.07
E 48996	26.00	0.00	14.09	18.40	4.88	4.23
E 48388	8.03	0.00	11.53	6.50	0.00	1.89
E 48389	5.09	0.00	5.74	3.51	0.00	0.82
E 48390	2.78	0.00	4.80	2.54	0.00	0.00
E 48214	4.13	0.00	5.93	3.15	0.00	0.74
E 48220	8.09	0.00	12.68	7.06	0.00	1.77
E 48393	2.85	0.00	4.56	2.47	0.00	0.62
E 48394	3.53	0.00	6.18	3.63	0.00	0.84
E 48396	3.90	0.00	5.05	2.49	0.00	0.75
E 48397	1.04	0.00	1.58	0.79	0.00	0.41
E 48398	1.01	0.00	0.96	0.44	0.00	0.20
E 48400	1.62	0.00	4.26	2.33	0.00	0.54
E 48401	0.00	0.00	0.25	0.12	0.00	0.00
E 48382	0.00	0.00	0.57	0.21	0.00	0.00
E 48383	5.95	0.00	6.30	3.73	0.00	1.32
E 48384	0.00	0.00	0.00	0.00	0.00	0.00
E 48985	137.51	41.53	1.71	77.78	0.00	4.98
E 48986	5.47	1.91	0.50	3.54	0.00	0.50
E 48987	3.12	1.17	0.21	1.95	0.00	19.80
E 48988	0.00	0.00	0.00	0.00	0.00	0.00
E 48989	0.17	0.34	0.00	0.25	0.00	0.03
E 48993	6.18	0.00	1.89	2.86	0.42	0.56
E 48991	0.00	0.00	0.24	0.13	0.00	0.07
E 48992	3.72	0.00	6.21	3.64	0.00	0.93

Table A.14: (continued)

Sample	Sum $\frac{\mu g}{gTOC}$
E 49710	322.48
E 48990	3.47
E 48996	394.15
E 48388	309.61
E 48389	161.52
E 48390	75.00
E 48214	146.00
E 48220	226.85
E 48393	82.83
E 48394	105.36
E 48396	79.15
E 48397	39.58
E 48398	17.05
E 48400	63.47
E 48401	5.08
E 48382	10.65
E 48383	212.20
E 48384	4.58
E 48985	2613.16
E 48986	92.09
E 48987	79.57
E 48988	5.89
E 48989	8.06
E 48993	80.50
E 48991	5.30
E 48992	118.15

Table A.15: Distribution of Hopanes

Sample	αTNH	βTNH	αDNH	α-βNH	$\beta\alpha$NM	2MH
	%	%	%	%	%	%
E 49748	35.1	0.0	26.4	0.0	69.2	32.1
E 49750	56.0	0.0	0.0	0.0	66.2	19.6
E 49751	0.0	0.0	0.0	0.0	0.0	8.0
E 48478	70.8	0.0	1.8	0.0	74.2	9.6
E 48479	100.0	0.0	4.7	0.0	62.0	10.6
E 48430	100.0	0.0	27.4	0.0	15.5	25.9
E 48425	69.5	0.0	18.8	0.0	41.2	21.9

Table A.15: (continued)

Sample	$\alpha\beta$H	$\beta\beta$NH	$\beta\alpha$M	$S\alpha\beta$HH	$R\alpha\beta$HH	S+$R\beta\alpha$HM
	%	%	%	%	%	%
E 49748	0.0	100.0	15.8	15.5	14.8	0.0
E 49750	0.0	100.0	24.7	0.0	68.9	43.5
E 49751	0.0	100.0	8.6	0.0	82.5	36.6
E 48478	0.0	100.0	0.0	16.0	29.7	17.9
E 48479	0.0	74.3	0.0	8.6	24.6	18.4
E 48430	0.0	99.0	46.3	0.0	47.3	24.9
E 48425	0.0	100.0	19.9	4.4	22.1	22.1

Table A.15: (continued)

Sample	$\beta\beta$H	$S\alpha\beta$DHH	$R\alpha\beta$DHH	$S + 22R\beta\alpha$DHM	THH	THH
	%	%	%	%	%	%
E 49748	0.0	0	55.9	0.0	0.0	0.0
E 49750	0.0	25.6	29.5	0.0	0.0	0.0
E 49751	0.0	17.9	55.1	0.0	0.0	0.0
E 48478	0.0	13.9	6.3	0.0	0.0	0.0
E 48479	0.0	16.8	7.3	0.0	0.0	0.0
E 48430	0.0	20.8	10.2	0.0	4.1	0.0
E 48425	0.0	8.0	9.3	0.0	2.2	0.0

Table A.16: Concentrations of Alkylhopenes

Sample	E 48985	E 48986	E 48987	E 48989
Compound	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$
hop-17(21)-ene	50.1	2.1	1.3	0.1
neohop-13(18)-ene	3.5	0.2	0.1	0.3
methylhopene	17.0	0.1	0.1	<0.1
22S-homohop-17(21)-ene	52.9	2.2	1.3	0.1
22R-homohop-17(21)-ene	125.9	4.4	2.8	0.5
22S-dihomohop-17(21)-ene	18.2	0.9	0.5	0.1
22R-dihomohop-17(21)-ene	19.9	1.0	0.6	0.1
22S-trihomohop-17(21)-ene	15.6	0.7	0.4	0.1
22R-trihomohop-17(21)-ene	4.9	0.3	0.2	<0.1
22S-tetrahomohop-17(21)-ene	20.9	0.6	0.3	0.1
22R-tetrahomohop-17(21)-ene	9.3	0.6	0.3	0.1
22S-pentahomohop-17(21)-ene	8.8	0.5	0.3	0.1
22R-pentahomohop-17(21)-ene	4.4	0.3	0.2	0.1
Sum	415.1	16.8	10.0	1.6
HomoHopeneIndex	0.05	0.07	0.06	0.10

Table A.17: Concentrations of Tetracyclic Secohopanes

Mass	330	330	344	358	358
Sample	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$
49710	1.25	0.0	0.34	0.0	0.0
48990	0.12	0.03	0.06	0.02	0.0
48996	0.28	0.87	0.60	3.08	1.34
48389	0.02	0.0	0.06	0.10	0.15
48214	0.33	0.0	0.13	0.0	0.0
48220	0.62	0.0	0.27	0.0	0.0
48394	0.26	0.0	0.14	0.0	0.0
48396	0.31	0.0	0.04	0.0	0.0
48400	0.15	0.0	0.05	0.0	0.0
48401	0.04	0.0	0.01	0.0	0.0
48382	0.15	0.0	0.02	0.0	0.0
48985	10.11	3.73	19.29	18.94	47.45
48986	1.10	0.36	1.74	1.58	3.64
48987	0.86	0.30	1.56	1.56	3.59
48989	0.02	0.0	0.06	0.10	0.15
48991	0.15	0.30	0.03	0.30	0.04
48992	3.66	2.33	1.78	6.37	1.31

A.3 Aromatic Hydrocarbons

Table A.18: Concentrations of Alkylnaphthalenes

Sample	N	2-MN	1-MN	2-EN	1-EN	2.6-DMN
	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$
E 49710	4.13	55.6	39.5	18.8	10.8	19.6
E 49890	0.01	0.10	0.37	0.03	0.08	0.16
E 49896	0.11	0.57	0.85	0.46	1.57	1.03
E 48388	46.74	419.51	338.44	20.88	18.41	68.00
E 48389	56.58	285.06	193.92	9.76	7.66	34.50
E 48390	76.58	439.75	262.54	15.57	11.51	46.45
E 48214	31.21	360.69	257.03	18.96	14.54	55.30
E 48216	54.96	433.19	314.37	16.10	13.84	68.18
E 48403	0.05	0.29	0.64	0.23	0.27	1.78
E 48220	0.11	8.18	13.58	3.13	1.93	17.86
E 48392	2.29	30.31	26.00	6.55	4.31	15.85
E 48393	0.35	11.14	18.83	4.25	4.27	11.11
E 48394	0.32	2.61	9.18	2.92	3.40	12.77
E 48395	0.40	5.49	10.99	5.99	1.36	8.09
E 48396	0.22	0.65	8.49	5.71	1.99	5.72
E 48397	0.00	0.12	0.00	0.10	0.21	0.82
E 48398	0.10	1.40	4.41	1.47	1.19	2.19
E 48400	0.80	20.49	34.95	4.14	3.82	9.27
E 48401	0.00	2.03	5.19	1.05	1.87	3.32
E 48405	6.75	103.74	45.91	5.01	2.26	16.19
E 48382	6.8	93.12	78.79	7.51	7.15	6.09
E 48383	7.79	133.37	170.09	12.23	10.59	31.84
E 48384	5.38	34.73	23.72	1.5	1.26	2.46
E 498985	0.00	0.00	0.00	19.12	17.95	61.98
E 48986	0.10	1.04	0.78	0.09	0.06	0.26
E 48987	0.04	0.27	0.21	0.04	0.02	0.09
E 48988	0.00	0.00	0.00	0.48	0.26	1.35
E 48989	6.64	36.07	18.66	1.67	0.64	3.50
E 48993	0.02	2.88	4.51	1.67	1.51	1.38
E 48991	0.67	148.71	137.45	25.53	19.66	73.18
E 48992	0.00	123.89	132.1	12.33	14.18	16.65

N:naphthalene, MN:methylnaphthalene
EN:ethylnaphthalene, DMN: dimethylnaphthalene

Table A.18: (continued)

Sample	2,7-DMN $\frac{\mu g}{gTOC}$	1,3 + 1,7-DMN $\frac{\mu g}{gTOC}$	1,3-DMN $\frac{\mu g}{gTOC}$	1,7-DMN $\frac{\mu g}{gTOC}$	1,6-DMN $\frac{\mu g}{gTOC}$	1,4 + 2,3-DMN $\frac{\mu g}{gTOC}$
E 49710	18.06	22.82	0.00	33.69	60.19	45.41
E 48990	0.25	1.03	0.00	1.96	1.39	1.27
E 48996	0.28	0.60	0.00	1.60	1.18	5.95
E 48388	81.92	205.60	0.00	0.00	143.53	114.96
E 48389	50.39	102.44	0.00	0.00	69.28	52.39
E 48390	59.45	123.31	0.00	0.00	79.55	61.33
E 48214	66.18	155.22	0.00	0.00	110.67	83.71
E 48216	63.66	174.91	0.00	0.00	116.59	91.22
E 48403	1.99	3.20	0.00	0.00	1.05	3.47
E 48220	13.62	32.50	0.00	0.00	19.59	30.33
E 48392	15.49	30.38	0.00	0.00	20.75	30.66
E 48393	11.61	26.59	0.00	0.00	20.09	28.70
E 48394	14.81	16.17	0.00	0.00	9.22	38.77
E 48395	8.84	15.10	0.00	0.00	9.53	15.04
E 48396	3.77	14.46	0.00	0.00	4.77	19.84
E 48397	0.68	1.07	0.00	0.00	0.61	2.34
E 48398	1.99	6.10	0.00	0.00	3.34	5.95
E 48400	10.91	34.67	0.00	0.00	22.11	21.67
E 48401	5.94	19.48	0.00	0.00	14.23	12.61
E 48405	28.75	36.53	0.00	0.00	23.56	13.04
E 48382	9.37	31.71	0.00	0.00	22.41	24.65
E 48383	32.75	102.00	0.00	0.00	84.34	62.19
E 48384	4.17	9.47	0.00	0.00	8.12	4.93
E 48985	72.63	168.81	0.00	0.00	167.32	105.65
E 48986	0.39	0.32	0.00	0.43	0.93	0.36
E 48987	0.16	0.10	0.00	0.18	0.33	0.15
E 48988	3.63	2.39	0.00	4.30	11.36	3.47
E 48989	4.28	3.95	0.00	4.35	7.68	3.59
E 48993	1.55	2.76	0.00	5.94	4.36	8.51
E 48991	79.74	88.00	0.00	119.24	174.10	143.47
E 48992	19.99	22.82	0.00	46.92	77.23	39.67

DMN:dimethylnaphthalene

Table A.18: (continued)

Sample	1,5-DMN $\frac{\mu g}{gTOC}$	1,2-DMN $\frac{\mu g}{gTOC}$	A-C_3-N $\frac{\mu g}{gTOC}$	B-C_3-N $\frac{\mu g}{gTOC}$	C-C_3-N $\frac{\mu g}{gTOC}$	D-C_3-N $\frac{\mu g}{gTOC}$
E 49710	14.31	25.44	5.85	9.77	5.92	3.76
E 48990	0.74	0.58	0.07	0.10	0.23	0.24
E 48996	0.65	1.78	0.78	0.88	2.52	2.59
E 48388	35.56	35.43	6.86	12.79	9.85	7.75
E 48389	15.60	14.58	3.32	5.75	3.64	3.51
E 48390	19.13	19.44	4.14	7.59	4.10	3.53
E 48214	26.85	27.61	6.63	10.62	7.31	5.53
E 48216	29.36	31.05	5.75	8.75	7.63	6.03
E 48403	0.90	1.17	0.58	2.25	0.91	0.64
E 48220	7.50	6.76	2.53	4.80	5.70	3.56
E 48392	9.30	7.93	2.03	4.27	2.78	1.80
E 48393	7.49	6.48	2.11	3.76	2.89	1.80
E 48394	6.74	4.22	3.02	4.25	4.39	2.73
E 48395	4.50	4.94	2.40	5.79	2.72	1.94
E 48396	6.83	7.43	2.84	4.83	3.90	2.16
E 48397	0.65	0.72	0.70	0.46	1.57	0.79
E 48398	2.15	2.00	1.07	2.86	1.49	1.08
E 48400	7.50	7.47	1.96	3.98	3.04	2.33
E 48401	5.76	5.81	1.07	3.82	2.49	2.16
E 48405	5.03	2.40	0.87	4.71	1.35	1.06
E 48382	7.57	11.63	2.13	5.46	2.22	1.75
E 48383	26.52	32.61	4.42	8.95	6.62	4.40
E 48384	2.42	2.89	0.44	1.72	0.61	0.37
E 48985	58.33	64.74	0.00	26.30	14.69	12.67
E 48986	0.25	0.37	0.02	0.10	0.06	0.04
E 48987	0.09	0.13	0.00	0.03	0.02	0.01
E 48988	1.86	1.18	0.00	0.00	0.00	0.00
E 48989	1.88	3.36	0.25	0.59	0.36	0.23
E 48993	3.30	4.05	0.76	1.03	1.24	1.18
E 48991	61.55	85.99	9.13	19.04	16.90	12.89
E 48992	27.26	39.90	2.73	7.16	4.16	2.48

DMN:dimethylnaphthalene, N:naphthalene

Table A.18: (continued)

Sample	E-C_3-N	F-C_3-N	G-C_3-N	1,3,7-TMN	1,3,6-TMN	1,3,5 + 1,4,6-TMN
	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$
E 49710	21.89	13.80	8.71	23.13	31.74	35.61
E 48990	0.33	0.47	0.28	3.12	3.37	4.06
E 48996	5.61	2.30	2.83	5.25	3.53	12.88
E 48388	28.74	20.55	3.26	97.24	106.67	81.88
E 48389	14.83	6.95	1.41	42.47	52.11	31.07
E 48390	17.13	9.34	1.04	47.58	50.72	34.92
E 48214	12.56	13.27	2.55	67.92	77.78	53.69
E 48216	26.23	13.71	2.56	87.22	94.75	72.13
E 48403	3.32	1.91	0.11	10.91	12.73	8.96
E 48220	16.75	8.33	1.34	40.64	43.00	34.92
E 48392	8.64	5.43	2.96	16.26	14.67	13.45
E 48393	8.82	5.91	1.11	17.09	16.35	15.03
E 48394	11.44	8.21	1.33	22.49	19.88	21.73
E 48395	8.76	3.8.0	0.76	13.50	12.58	8.65
E 48396	8.85	5.17	0.93	15.93	11.69	15.24
E 48397	2.92	2.49	0.13	4.76	3.69	6.34
E 48398	3.54	2.15	0.33	6.33	4.71	5.78
E 48400	9.78	5.07	0.83	22.30	24.49	19.78
E 48401	6.85	5.89	0.88	22.14	24.00	22.48
E 48405	6.36	3.43	0.23	13.33	15.29	6.74
E 48382	5.35	4.02	0.88	8.43	8.04	6.85
E 48383	21.48	9.11	1.77	39.37	48.69	40.59
E 48384	1.34	0.91	0.08	2.68	3.36	2.46
E 48985	96.27	59.6	26.12	199.93	279.74	220.99
E 48986	0.14	0.11	0.06	0.57	0.78	0.68
E 48987	0.08	0.06	0.03	0.24	0.29	0.23
E 48988	0.00	0.00	0.00	6.52	6.75	10.18
E 48989	0.80	0.73	0.43	2.91	3.52	3.08
E 48993	1.96	1.55	2.44	3.46	4.75	8.87
E 48991	56.09	33.13	20.02	109.54	148.18	158.26
E 48992	9.21	10.59	4.41	13.18	20.80	35.40

N:naphthalene, TMN:trimethylnaphthalene

Table A.18: (continued)

Sample	2,3,6-TMN $\frac{\mu g}{gTOC}$	1,2,7-TMN $\frac{\mu g}{gTOC}$	1,6,7-TMN $\frac{\mu g}{gTOC}$	1,2,6-TMN $\frac{\mu g}{gTOC}$	1,2,4-TMN $\frac{\mu g}{gTOC}$	1,2,5-TMN $\frac{\mu g}{gTOC}$
E 49710	32.37	14.29	36.99	35.36	13.91	162.94
E 48990	2.15	1.57	2.63	1.24	0.66	3.38
E 48996	4.18	2.99	23.71	1.91	3.01	5.96
E 48388	102.75	17.31	71.08	45.24	9.92	42.60
E 48389	49.63	7.51	29.9	14.6	3.91	11.46
E 48390	50.17	8.34	29.41	16.65	4.55	12.85
E 48214	74.57	14.33	49.84	31.67	7.73	26.95
E 48216	89.51	15.43	59.54	34.31	10.73	31.39
E 48403	9.25	1.21	6.32	2.92	0.60	2.75
E 48220	55.20	9.53	36.20	15.34	5.48	17.48
E 48392	20.36	6.33	17.38	8.93	2.06	11.56
E 48393	20.97	4.97	18.09	8.97	2.42	13.00
E 48394	31.71	8.43	28.53	10.49	3.05	21.27
E 48395	15.11	2.43	10.67	8.16	1.44	6.77
E 48396	16.06	5.23	17.74	10.34	3.11	15.49
E 48397	8.11	3.02	7.97	6.30	1.16	13.46
E 48398	5.96	1.98	5.81	3.38	1.33	4.98
E 48400	23.37	4.76	18.79	10.33	3.05	12.85
E 48401	25.36	5.54	20.39	15.96	4.24	16.68
E 48405	13.77	1.22	5.64	2.27	0.59	1.11
E 48382	8.40	2.89	10.06	6.23	2.02	9.99
E 48383	45.87	15.85	41.72	49.58	9.24	127.81
E 48384	2.60	0.84	2.65	3.09	0.55	5.04
E 48985	242.58	188.53	182.98	191.69	45.52	528.50
E 48986	0.54	1.46	0.42	0.64	0.08	2.03
E 48987	0.24	0.23	0.20	0.24	0.04	0.76
E 48988	5.28	3.54	16.37	3.18	0.00	38.83
E 48989	2.95	6.59	2.24	2.91	0.52	6.81
E 48993	4.30	4.36	7.69	5.05	4.66	10.15
E 48991	163.47	62.29	138.31	153.23	36.90	211.53
E 48992	17.02	22.19	24.12	42.58	9.30	237.11

TMN:trimethylnaphthalene

Table A.18: (continued)

Sample	H-C_4-N $\frac{\mu g}{gTOC}$	I-C_4-N $\frac{\mu g}{gTOC}$	J-C_4-N $\frac{\mu g}{gTOC}$	1,3,5,7-TeMN $\frac{\mu g}{gTOC}$	1,3,6,7-TeMN $\frac{\mu g}{gTOC}$	K-TeMN $\frac{\mu g}{gTOC}$
E 49710	11.45	0.00	0.00	1.64	4.71	22.64
E 48990	0.00	0.00	0.00	0.58	2.01	1.87
E 48996	4.08	1.34	7.68	7.75	10.83	13.59
E 48388	9.00	2.49	16.10	19.43	44.99	25.62
E 48389	4.16	1.49	8.12	8.43	18.92	8.98
E 48390	3.99	1.02	5.20	8.65	17.15	9.38
E 48214	6.94	2.78	13.69	15.92	30.04	16.72
E 48216	8.32	4.09	15.53	17.44	42.26	26.01
E 48403	1.18	0.41	1.38	2.13	4.36	1.94
E 48220	6.40	2.95	12.05	14.06	29.97	18.32
E 48392	1.87	1.07	3.74	5.36	7.86	4.66
E 48393	1.98	1.51	4.04	5.85	9.39	6.14
E 48394	3.71	2.36	7.10	9.39	16.28	10.56
E 48395	1.87	0.69	3.56	3.79	5.33	2.75
E 48396	2.38	4.03	4.61	6.17	8.20	6.14
E 48397	1.38	2.61	2.79	1.48	6.07	5.45
E 48398	1.11	2.07	2.31	3.08	4.08	3.10
E 48400	2.87	1.32	5.05	6.99	13.04	7.74
E 48401	4.40	2.16	7.75	10.20	19.90	13.64
E 48405	1.00	0.26	1.05	1.60	2.46	0.96
E 48382	0.88	0.47	2.13	3.16	3.22	2.30
E 48383	4.72	2.40	9.79	13.33	19.41	17.28
E 48384	0.23	0.12	0.50	0.77	1.06	1.00
E 48985	0.00	0.00	0.00	104.18	217.41	188.09
E 48986	0.00	0.00	0.00	0.23	0.18	0.45
E 48987	0.00	0.00	0.05	0.00	0.00	0.00
E 48988	0.00	0.00	0.00	3.80	8.80	9.97
E 48989	0.00	0.00	0.00	0.82	0.00	1.10
E 48993	4.61	0.00	1.17	3.96	6.26	7.27
E 48991	0.00	0.00	9.44	39.54	98.63	89.58
E 48992	2.76	1.23	2.40	4.90	12.51	13.47

N:naphthalene, TeMN:tetramethylnaphthalene
K-TeMN = 1,2,4,6- + 1,2,4,7- + 1,4,6,7-TeMN

Table A.18: (continued)

Sample	1,2,5,7-TeMN $\frac{\mu g}{gTOC}$	2,3,6,7-TeMN $\frac{\mu g}{gTOC}$	,1,2,6,7-TeMN $\frac{\mu g}{gTOC}$	1,2,3,7-TeMN $\frac{\mu g}{gTOC}$	1,2,3,6-TeMN $\frac{\mu g}{gTOC}$	L-TeMN $\frac{\mu g}{gTOC}$
E 49710	19.59	4.19	13.64	6.54	18.33	99.25
E 48990	1.28	0.47	0.94	0.55	0.97	1.33
E 48996	5.15	3.28	5.69	3.00	5.21	22.50
E 48388	13.81	11.77	18.09	6.66	16.72	25.00
E 48389	4.68	6.22	6.20	3.12	6.63	7.32
E 48390	4.01	5.24	5.59	2.62	4.88	7.78
E 48214	8.87	9.61	11.63	5.66	12.70	16.52
E 48216	12.21	13.53	14.83	6.65	16.51	20.30
E 48403	0.75	1.45	0.86	0.47	1.08	0.93
E 48220	9.38	9.90	11.83	5.68	13.14	16.46
E 48392	3.19	1.70	3.75	1.72	3.29	4.90
E 48393	3.55	2.40	4.15	2.19	4.58	7.70
E 48394	6.62	4.35	6.99	3.44	7.02	13.05
E 48395	2.05	1.89	2.86	1.24	3.15	4.59
E 48396	4.59	2.48	5.40	2.37	5.43	10.38
E 48397	4.99	1.50	4.83	1.92	4.11	15.34
E 48398	2.40	1.50	2.88	1.32	2.70	4.97
E 48400	4.60	3.58	6.36	2.30	5.60	9.88
E 48401	8.63	6.76	11.29	4.73	10.82	19.25
E 48405	0.32	1.07	0.79	0.55	0.59	0.27
E 48382	1.82	0.82	2.73	0.90	2.55	6.05
E 48383	15.62	5.96	16.21	6.09	17.25	60.09
E 48384	1.08	0.33	1.06	0.34	0.95	4.10
E 48985	130.83	49.75	124.38	115.10	184.22	354.39
E 48986	0.43	0.19	0.38	0.32	0.39	1.46
E 48987	0.13	0.00	0.00	0.00	0.14	0.41
E 48988	0.00	0.00	0.00	0.00	0.00	0.00
E 48989	0.96	0.47	0.96	0.64	0.88	3.32
E 48993	5.28	1.35	4.40	2.60	5.00	32.72
E 48991	76.53	33.58	79.37	32.73	80.76	166.36
E 48992	28.23	13.20	4.09	3.89	10.95	103.91

TeMN:tetramethylnaphthalene
L-TeMN = 1,2,5,6- + 1,2,3,5-TeMN

Table A.18: (continued)

Sample	Cadalene $\frac{\mu g}{gTOC}$	SUM $\frac{\mu g}{gTOC}$
E 49710	19.27	1045.66
E 48990	0.27	42.12
E 48996	6.82	194.47
E 48388	4.55	2407.72
E 48389	1.99	1260.50
E 48390	1.78	1593.93
E 48214	3.28	1825.30
E 48216	4.05	2174.85
E 48403	0.34	97.68
E 48220	3.17	609.21
E 48392	0.83	382.66
E 48393	1.87	349.57
E 48394	2.32	417.27
E 48395	1.06	230.58
E 48396	0.90	282.46
E 48397	0.43	124.10
E 48398	0.71	117.30
E 48400	1.50	415.34
E 48401	2.24	379.00
E 48405	0.23	378.25
E 48382	0.54	419.12
E 48383	2.37	1372.32
E 48384	0.11	141.42
E 48985	237.24	4758.26
E 48986	3.50	20.62
E 48987	0.47	5.67
E 48988	0.00	143.50
E 48989	9.62	149.98
E 48993	8.51	189.01
E 48991	15.29	3228.00
E 48992	0.00	1236.93

Table A.19: Distribution of Alkylnaphthalenes (samples without standard)

Sample	N	2-MN	1-MN	2-EN	1-EN	2,6-DMN
	%	%	%	%	%	%
E 48478	0.6	11.8	15.3	2.9	4.0	8.9
E 48479	2.2	35.4	40.1	3.7	4.3	15.3
E 49749	100.0	90.0	44.9	0.0	0.0	3.8
E 49748	52.6	81.0	56.8	7.1	7.1	8.5
E 49750	100.0	72.5	40.4	2.5	0.0	1.6
E 49751	6.8	70.6	75.0	11.7	17.8	31.6
E 48430	3.5	100.0	91.4	14.0	11.2	33.5
E 48425	0.0	0.0	12.7	0.0	0.0	12.2

N:naphthalene, MN:methylnaphthalene
EN:ethylnaphthalene, DMN:dimethylnaphthalene

Table A.19: (continued)

Sample	2,7-DMN	1,3-DMN	1,7-DMN	1,6-DMN	1,4 + 2,3-DMN	1,5-DMN
	%	%	%	%	%	%
E 48478	16.5	28.4	0.0	36.3	21.0	16.6
E 48479	16.9	43.7	0.0	82.1	18.7	22.7
E 49749	3.7	3.9	6.4	15.5	7.5	0.8
E 49748	9.6	9.4	15.1	23.1	16.4	7.6
E 49750	1.6	0.0	0.0	6.8	2.6	0.3
E 49751	40.3	42.9	68.7	97.8	56.1	28.6
E 48430	28.3	54.1	56.1	77.3	82.6	26.8
E 48425	30.3	12.4	19.6	33.0	21.0	7.0

DMN:dimethylnaphthalene

Table A.19: (continued)

Sample	1,2-DMN	A-C_3-N	B-C_3-N	C-C_3-N	D-C_3-N	E-C_3-N
	%	%	%	%	%	%
E 48478	8.0	1.7	4.3	3.5	2.6	7.3
E 48479	15.9	1.5	4.3	3.7	3.1	7.4
E 49749	0.0	0.0	0.0	0.0	0.0	0.0
E 49748	10.3	1.9	0.0	2.3	1.9	2.1
E 49750	0.9	0.0	0.0	0.0	0.0	0.0
E 49751	35.5	5.0	16.0	7.2	6.6	5.2
E 48430	32.0	7.2	9.6	9.5	6.6	12.2
E 48425	4.5	0.0	0.0	0.0	0.0	13.1

N:naphthalene, DMN:dimethylnaphthalene

Table A.19: (continued)

Sample	F-C_3-N	G-C_3-N	1,3,7-TMN	1,3,6-TMN	1,3,5 + 1,4,6-TMN	2,3,6 TMN
	%	%	%	%	%	%
E 48478	9.3	4.1	23.6	43.6	31.9	33.5
E 48479	7.4	0.0	38.8	78.8	58.3	36.0
E 49748	2.5	2.3	3.9	7.2	10.6	8.0
E 49749	0.0	0.0	0.0	2.4	0.6	0.0
E 49750	0.0	0.0	0.0	0.4	0.6	0.9
E 49751	7.6	4.8	9.1	27.1	45.9	35.8
E 48430	10.0	9.8	21.5	15.0	36.7	59.2
E 48425	14.6	2.8	32.9	54.4	18.8	72.3

N:naphthalene, TMN:trimethylnaphthalene

Table A.19: (continued)

Sample	1,2,7-TMN	1,6,7-TMN	1,2,6-TMN	1,2,4-TMN	1,2,5-TMN	H-C_4-N
	%	%	%	%	%	%
E 48478	7.5	27.0	31.5	5.9	51.4	6.0
E 48479	13.9	30.8	58.2	9.7	98.9	9.4
E 49748	4.5	6.8	8.4	3.5	22.1	1.4
E 49749	0.0	1.9	3.7	0.0	18.1	0.0
E 49750	0.0	0.6	1.3	0.0	8.1	0.0
E 49751	17.5	32.3	29.3	9.7	54.8	6.9
E 48430	22.6	63.8	27.3	2.6	87.6	0.0
E 48425	0.0	25.1	0.0	0.0	100.0	0.0

TMN:trimethylnaphthalene, N:naphthalene

Table A.19: (continued)

Sample	I-C_4-N	J-C_4-N	1,3,5,7-TeMN	1,3,6,7-TeMN	K-TeMN	1,2,5,7-TeMN
	%	%	%	%	%	%
E 48478	0.0	9.4	11.0	29.6	31.7	34.1
E 48479	0.0	13.3	35.4	37.8	50.4	46.6
E 49748	0.0	4.1	1.4	0.0	7.5	5.9
E 49749	0.0	0.0	1.2	0.0	12.0	7.7
E 49750	0.0	0.0	2.3	0.0	9.6	7.2
E 49751	0.0	0.0	3.0	18.4	16.8	15.5
E 48430	0.0	0.0	0.0	0.0	0.0	0.0
E 48425	0.0	0.0	0.0	21.0	0.0	0.0

N:naphthalene, TeMN:tetramethylnaphthalene
K-TeMN = 1,2,4,6- + 1,2,4,7- + 1,4,6,7-TeMN

Table A.19: (continued)

Sample	2,3,6,7-TeMN	,1,2,6,7-TeMN	1,2,3,7-TeMN	1,2,3,6-TeMN	L-TeMN	Cadalene
	%	%	%	%	%	%
E 48425	0.0	0.0	0.0	0.0	0.0	0.0
E 48430	0.0	0.0	0.0	0.0	0.0	0.0
E 49751	5.1	11.8	4.6	18.6	36.6	10.9
E 49750	1.8	8.1	2.9	25.8	58.4	0.0
E 49749	0.0	9.3	2.4	24.7	70.7	0.0
E 49748	0.0	4.4	1.6	10.3	18.5	9.2
E 48478	11.7	25.1	17.6	49.5	100.0	2.9
E 48479	12.5	31.5	21.8	49.0	100.0	0.0

TeMN:tetramethylnaphthalene
L-TeMN = 1,2,5,6- + 1,2,3,5-TeMN

Table A.20: Ratios of Alkylnaphthalenes

Sample	TNR1	TNR2	TNNr	TeMN	TrMN
E 49710	0.91	0.82	0.12	0.05	0.23
E 49748	0.76	0.67	0.15	0.00	0.25
E 49749	-	-	-	-	-
E 49750	-	-	-	-	-
E 49751	0.78	0.61	0.14	0.33	0.28
E 48990	0.53	0.71	0.48	0.60	0.39
E 48478	1.05	0.76	0.31	0.23	0.39
E 48479	0.62	0.55	0.28	0.27	0.36
E 48480	-	-	-	-	-
E 48996	0.32	0.57	0.47	0.32	0.20
E 48388	1.25	1.06	0.70	0.64	0.53
E 48389	1.60	1.11	0.79	0.72	0.59
E 48390	1.44	1.14	0.79	0.69	0.58
E 48214	1.39	1.08	0.72	0.65	0.54
E 48216	1.24	1.06	0.74	0.68	0.55
E 48430	1.61	1.56	0.20	??	0.28
E 48403	1.03	0.93	0.80	0.82	0.59
E 48392	1.51	1.30	0.58	0.62	0.46
E 48393	1.40	1.21	0.57	0.55	0.47
E 48394	1.46	1.30	0.51	0.56	0.44
E 48395	1.75	1.35	0.67	0.54	0.52
E 48396	1.05	1.19	0.51	0.44	0.39
E 48397	1.28	1.28	0.26	0.28	0.30
E 48398	1.03	1.17	0.56	0.45	0.42
E 48400	1.18	1.03	0.63	0.57	0.50
E 48401	1.13	1.02	0.57	0.51	0.46
E 48405	2.04	1.23	0.92	0.90	0.71
E 48425	-	-	-	-	-
E 48382	1.23	1.13	0.46	0.35	0.40
E 48383	1.13	0.95	0.24	0.24	0.32
E 48384	1.06	0.91	0.35	0.21	0.37
E 48985	1.10	0.88	0.27	0.38	0.35
E 48986	0.78	0.76	0.22	0.11	0.26
E 48987	1.04	0.92	0.24	-	0.31
E 48988	0.52	0.70	0.14	1.00	0.20
E 48989	0.96	0.89	0.30	-	0.30
E 48993	0.49	0.57	0.25	0.16	0.23
E 48991	1.03	0.89	0.34	0.37	0.36
E 48992	0.48	0.54	0.05	0.11	0.12

for abbreviation of ratios see Table 6.4

Table A.21: Concentrations of Alkylphenanthrenes

Sample	P	3-MP	2-MP	9-MP	1-MP	3-EP	2-EP
	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$
E 49710	36.4	37.6	54.6	46.9	2.7	5.2	3.5
E 48990	13.3	12.2	16.9	15.4	24.4	1.1	1.0
E 48996	40.4	18.8	20.7	28.7	20.5	7.5	3.7
E 48388	174.8	96.7	116.7	116.8	98.6	11.3	7.2
E 48389	101.9	61.9	73.5	70.3	49.4	5.5	3.3
E 48390	127.7	52.9	68.2	61.6	44.6	5.3	3.5
E 48214	195.9	71.0	86.9	85.2	65.3	7.9	4.4
E 48216	155.0	89.3	106.1	111.7	79.9	9.7	6.1
E 48403	53.9	98.6	86.1	74.1	45.4	5.3	1.2
E 48220	101.9	87.1	88.5	111.9	72.7	10.1	6.9
E 48392	105.5	26.6	31.5	45.4	30.3	3.4	2.2
E 48393	84.8	24.5	28.8	44.2	27.6	3.4	2.4
E 48394	141.9	41.0	46.0	76.6	45.8	6.0	3.9
E 48395	94.3	29.8	33.4	45.5	26.1	3.5	2.5
E 48396	91.4	30.3	33.4	49.8	34.5	4.5	3.0
E 48397	51.6	30.2	24.8	40.7	31.3	4.5	4.4
E 48398	60.5	25.1	24.3	35.1	21.2	3.7	2.5
E 48400	68.1	41.2	46.8	58.4	40.3	5.9	3.4
E 48401	184.7	87.1	101.6	153.7	97.0	13.3	9.1
E 48405	265.8	113.5	141.6	70.7	49.9	5.1	0.9
E 48382	202.3	45.7	62.5	94.1	51.3	4.7	4.2
E 48383	138.3	88.1	111.3	128.1	101.4	8.8	4.3
E 48384	39.5	10.2	12.1	18.8	11.4	0.9	0.9
E 48985	10550	5636	7586	2238	1895	317	175
E 48986	45.5	3.9	4.8	3.0	3.9	0.2	0.1
E 48987	38.4	3.9	5.4	2.7	4.3	0.2	0.1
E 48988	90.8	39.4	46.9	83.3	51.7	8.1	0.8
E 48989	105.1	7.4	8.8	5.2	6.4	0.4	0.2
E 48993	22.0	10.9	10.8	11.4	11.0	2.8	1.8
E 48991	866.7	424.2	480.9	537.6	501.0	52.2	53.8
E 48992	227.3	77.5	84.4	142.9	117.2	9.7	12.1

P:phenanthrene, MP:methylphenanthrene
EP:ethylphenanthrene

Table A.21: (continued)

Sample	3,6-DMP	9-EP	2,6-DMP	2,7-DMP	1,3- + 2,10- + 3,9-3,10-DMP	1,6-2,9-DMP
	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$
E 49710	2.8	6.2	4.5	39.9	10.1	9.5
E 48990	4.4	2.7	3.9	3.2	16.8	5.7
E 48996	6.9	2.2	2.2	2.3	19.9	7.7
E 48388	27.7	9.1	22.5	14.7	110.9	56.4
E 48389	15.8	3.7	14.0	9.8	67.0	31.3
E 48390	14.2	3.7	11.2	8.5	59.0	32.5
E 48214	17.9	6.4	13.7	9.0	68.9	36.1
E 48216	25.9	6.1	22.5	15.2	124.6	59.1
E 48403	18.3	0.7	24.6	21.7	86.8	39.1
E 48220	24.4	6.9	18.7	13.2	113.4	53.5
E 48392	6.5	3.3	3.7	2.6	21.5	12.6
E 48393	6.7	2.7	4.2	3.0	24.4	14.3
E 48394	12.3	4.3	6.8	5.1	43.0	21.8
E 48395	7.7	3.3	4.0	2.3	23.2	11.5
E 48396	8.9	3.9	4.2	3.2	26.6	13.6
E 48397	7.7	5.2	4.0	2.5	27.9	13.3
E 48398	8.3	2.9	3.7	2.2	22.0	11.3
E 48400	13.4	4.0	8.0	5.6	50.1	26.0
E 48401	30.7	12.9	19.9	11.8	114.5	57.0
E 48405	17.4	n.d.	19.8	15.4	53.2	26.1
E 48382	10.7	3.8	4.3	3.1	27.6	12.6
E 48383	21.6	6.9	14.8	10.9	76.8	40.8
E 48384	2.1	1.0	1.3	0.9	9.4	4.5
E 48985	352	818	1492	1032	2002	1288
E 48986	0.2	0.2	0.4	0.3	1.4	0.9
E 48987	0.4	0.4	0.6	0.5	1.9	1.3
E 48988	8.9	9.6	11.0	10.7	89.0	98.0
E 48989	0.6	0.6	0.8	0.5	2.4	1.7
E 48993	3.5	1.9	1.0	0.8	11.9	12.7
E 48991	39.4	44.2	84.9	64.3	466.0	147.1
E 48992	11.1	12.4	6.8	4.3	62.0	32.7

n.d.:not detected
DMP:dimethylphenanthrene, EP:ethylphenanthrene

Table A.21: (continued)

Sample	1,7-DMP $\frac{\mu g}{gTOC}$	2,3-DMP $\frac{\mu g}{gTOC}$	1,9- + 4,6-DMP $\frac{\mu g}{gTOC}$	1,8-DMP $\frac{\mu g}{gTOC}$	A-C_3-P $\frac{\mu g}{gTOC}$	B-C_3-P $\frac{\mu g}{gTOC}$	C-C_3-P $\frac{\mu g}{gTOC}$
E 49710	62.9	29.4	n.d.	19.4	n.d.	n.d.	n.d.
E 48990	19.7	3.4	7.0	4.2	n.d.	n.d.	2.3
E 48996	4.2	6.6	8.3	n.d.	n.d	n.d.	3.4
E 48388	36.7	34.1	27.4	19.3	6.1	2.1	8.8
E 48389	20.6	21.1	13.0	8.7	2.6	0.8	4.5
E 48390	13.4	17.3	11.8	7.5	2.3	0.9	3.8
E 48214	20.5	20.2	16.8	11.1	3.6	1.3	4.8
E 48216	31.7	35.4	26.6	16.2	4.6	2.2	8.2
E 48403	28.9	16.9	14.1	3.7	1.2	0.2	3.1
E 48220	23.3	28.9	25.1	14.5	3.6	2.4	7.2
E 48392	6.6	6.1	6.7	4.1	1.6	0.5	1.7
E 48393	8.7	6.4	6.6	4.3	4.2	0.6	1.9
E 48394	12.7	11.1	14.4	6.4	4.8	0.9	3.8
E 48395	4.7	5.8	6.4	3.2	0.8	0.6	1.9
E 48396	7.7	7.2	8.3	4.8	1.3	1.0	2.6
E 48397	8.3	6.1	9.7	5.0	1.0	1.5	2.1
E 48398	5.0	4.2	6.9	3.6	1.0	0.6	1.9
E 48400	11.7	12.4	11.8	7.6	1.8	1.0	4.1
E 48401	27.2	27.1	34.2	16.6	5.9	2.8	9.2
E 48405	14.1	14.7	5.8	2.7	0.9	0.1	2.1
E 48382	6.7	7.9	9.0	5.3	1.5	1.1	2.4
E 48383	26.1	20.7	22.9	13.2	3.3	1.6	5.8
E 48384	3.4	1.8	3.5	1.4	0.2	0.4	0.5
E 48985	845	429	363	n.d.	n.d.	n.d.	n.d.
E 48986	1.3	0.3	0.3	0.2	n.d.	n.d.	n.d.
E 48987	1.9	0.4	0.4	n.d.	n.d.	n.d.	n.d.
E 48988	36.9	19.3	37.4	n.d.	n.d.	n.d.	n.d.
E 48989	1.9	0.4	0.7	0.5	n.d.	n.d.	n.d.
E 48993	4.9	3.9	2.7	4.5	4.6	n.d.	n.d.
E 48991	192.9	137.4	150.7	125.6	22.6	n.d.	37.7
E 48992	33.8	14.5	26.1	21.2	n.d.	n.d.	4.3

n.d.:not detected

DMP:dimethylphenanthrene, P:phenanthrene

Table A.21: (continued)

Sample	D-C_3-P $\frac{\mu g}{gTOC}$	E-C_3-P $\frac{\mu g}{gTOC}$	F-C_3-P $\frac{\mu g}{gTOC}$	G-C_3-P $\frac{\mu g}{gTOC}$	H-C_3-P $\frac{\mu g}{gTOC}$	I-C_3-P $\frac{\mu g}{gTOC}$	J-C_3-P $\frac{\mu g}{gTOC}$
E 49710	7.1	21.5	20.5	2.3	10.6	15.4	n.d.
E 48990	1.1	5.0	0.6	n.d.	3.6	n.d.	46.5
E 48996	2.3	7.2	13.0	n.d.	n.d.	n.d	9.0
E 48388	6.3	20.2	8.9	2.1	23.7	14.4	50.3
E 48389	3.6	11.8	6.1	1.2	12.1	10.2	30.1
E 48390	3.0	9.4	2.7	0.8	10.0	5.9	20.8
E 48214	3.8	11.4	4.7	1.5	11.1	8.3	26.8
E 48216	6.7	18.4	6.8	2.6	27.2	13.9	54.6
E 48403	2.9	10.2	0.9	0.1	13.1	5.5	29.6
E 48220	6.5	18.1	3.3	2.7	20.5	11.0	43.7
E 48392	1.4	4.2	1.1	0.4	2.1	2.2	7.2
E 48393	1.7	5.6	2.0	1.2	3.5	2.6	10.1
E 48394	3.2	9.0	1.9	1.3	5.2	4.2	18.2
E 48395	1.2	4.5	0.9	0.2	2.5	2.7	5.8
E 48396	2.1	6.0	1.2	0.5	3.3	3.2	8.6
E 48397	1.4	6.4	1.7	0.2	3.9	3.5	9.1
E 48398	1.3	5.1	0.8	0.3	3.3	2.6	7.0
E 48400	2.8	9.9	2.5	1.0	8.2	4.9	17.9
E 48401	6.6	25.1	6.6	1.8	20.4	14.8	45.8
E 48405	2.0	6.0	0.6	n.d.	7.1	4.2	13.5
E 48382	1.5	6.0	1.6	0.3	2.0	3.1	8.0
E 48383	5.1	15.5	2.8	1.5	10.4	9.2	30.9
E 48384	0.3	1.7	0.4	n.d.	1.4	1.0	3.4
E 48985	141	340	50	n.d.	563	n.d.	958
E 48986	0.1	0.2	n.d.	n.d.	0.2	n.d.	0.7
E 48987	0.1	0.2	0.1	n.d.	0.4	0.1	1.2
E 48988	6.0	21.5	20.3	n.d.	35.9	18.4	57.3
E 48989	n.d.	0.3	0.1	n.d.	0.4	0.2	1.3
E 48993	2.0	2.9	n.d.	n.d.	n.d.	1.9	15.8
E 48991	32.5	103.8	29.1	n.d.	121.4	n.d.	241.3
E 48992	2.6	14.4	2.6	n.d.	7.4	n.d.	15.6

n.d.:not detected
P:phenanthrene

Table A.21: (continued)

Sample	K-C_3-P $\frac{\mu g}{gTOC}$	L-C_3-P $\frac{\mu g}{gTOC}$	M-C_3-P $\frac{\mu g}{gTOC}$	N-C_3-P $\frac{\mu g}{gTOC}$	O-C_3-P $\frac{\mu g}{gTOC}$	P-C_3-P $\frac{\mu g}{gTOC}$	Q-C_3-P $\frac{\mu g}{gTOC}$
E 49710	n.d.	6.3	33.8	12.0	8.5	n.d.	n.d.
E 48990	n.d.	0.9	7.1	1.5	1.2	1.3	1.1
E 48996	n.d.	0.5	7.4	4.2	1.5	0.8	n.d.
E 48388	10.4	7.2	36.8	12.7	9.6	9.1	8.3
E 48389	6.9	3.5	20.3	8.3	6.7	5.1	5.3
E 48390	6.4	2.8	14.3	6.1	3.6	4.0	3.7
E 48214	6.1	3.2	18.4	6.9	4.9	4.8	4.3
E 48216	20.0	7.4	40.1	16.1	9.8	10.7	9.3
E 48403	n.d.	2.6	14.0	6.3	2.8	4.2	4.9
E 48220	17.3	6.1	31.7	12.6	7.2	8.3	8.5
E 48392	2.2	0.8	4.8	1.9	1.6	1.1	1.1
E 48393	3.3	1.2	7.1	2.7	2.5	1.4	1.2
E 48394	5.4	2.2	12.5	4.6	3.8	2.9	2.9
E 48395	1.2	0.9	3.6	1.1	1.0	1.1	1.2
E 48396	2.7	1.2	6.8	2.3	1.7	1.6	1.7
E 48397	1.6	1.8	6.2	1.3	1.8	1.4	1.9
E 48398	1.3	1.0	4.5	1.3	1.3	1.1	1.5
E 48400	5.3	2.6	13.0	4.4	3.0	3.4	3.3
E 48401	8.8	6.5	29.9	8.6	8.1	7.6	7.6
E 48405	n.d.	0.9	3.1	3.5	1.3	1.3	n.d.
E 48382	1.6	1.5	4.4	1.2	1.3	1.3	2.6
E 48383	6.4	3.3	19.0	6.7	5.8	5.3	5.8
E 48384	0.3	0.6	2.3	0.4	0.6	0.6	0.6
E 48985	n.d.	59.6	450.2	129.0	72.1	107.7	n.d.
E 48986	n.d.	n.d.	0.3	n.d.	0.1	n.d.	n.d.
E 48987	n.d	n.d.	0.4	0.1	0.1	0.1	n.d.
E 48988	n.d.	6.9	43.6	11.3	6.6	11.6	8.1
E 48989	n.d.	0.1	0.5	0.1	0.2	0.1	n.d.
E 48993	n.d.	n.d.	4.9	n.d.	1.8	0.8	n.d.
E 48991	n.d.	31.3	201.9	58.6	43.8	50.9	37.4
E 48992	n.d.	n.d.	15.5	n.d.	4.8	3.4	3.6

n.d.:not detected
P:phenanthrene

Table A.21: (continued)

Sample	R-C_3-P	S-C_3-P	T-C_3-P	1,2,8-TMP	Retene	U-C_4-P	V-C_4-P
	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$
E 49710	n.d.	n.d.	25.4	28.9	21.1	8.6	4.2
E 48990	n.d.	2.6	8.0	1.7	32.9	0.8	0.4
E 48996	n.d.	8.2	3.3	n.d.	6.1	n.d.	1.8
E 48388	18.0	6.1	21.6	16.0	17.0	5.5	2.4
E 48389	11.3	3.4	10.7	8.3	5.5	4.1	1.2
E 48390	7.6	2.0	7.6	4.8	4.8	2.1	0.9
E 48214	9.8	3.2	10.4	7.8	9.7	2.7	1.8
E 48216	21.7	5.4	20.1	16.0	13.8	6.2	3.0
E 48403	6.3	1.0	3.2	1.4	n.d.	n.d.	n.d.
E 48220	14.2	5.8	17.5	15.1	12.3	3.9	2.5
E 48392	2.6	0.8	4.0	2.6	7.6	0.7	0.3
E 48393	3.2	1.2	6.7	3.3	18.2	1.1	0.5
E 48394	6.0	2.6	11.0	5.9	27.2	1.8	0.9
E 48395	1.6	0.7	2.1	1.9	2.3	0.5	0.3
E 48396	3.3	1.0	3.9	4.1	2.3	1.0	0.5
E 48397	3.0	1.1	3.6	7.2	2.8	0.8	0.5
E 48398	2.1	0.8	2.5	2.6	1.9	0.6	0.4
E 48400	6.2	2.1	8.4	6.7	7.5	1.8	1.1
E 48401	15.2	4.9	18.4	15.4	27.8	5.4	2.1
E 48405	n.d.	n.d.	1.0	0.4	n.d.	n.d.	n.d.
E 48382	2.2	0.9	2.9	3.6	3.9	0.5	0.3
E 48383	9.6	3.6	12.5	22.1	9.5	2.3	1.1
E 48384	0.9	0.3	1.1	2.9	0.4	0.2	0.1
E 48985	n.d.	n.d.	171.6	532.4	570.9	30.2	12.2
E 48986	n.d.	0.1	n.d.	0.3	2.1	n.d.	n.d.
E 48987	n.d.	0.1	n.d.	0.4	7.2	n.d.	n.d.
E 48988	n.d.	n.d.	6.6	n.d.	13.0	3.4	2.5
E 48989	n.d.	n.d.	n.d.	0.5	4.2	n.d.	n.d.
E 48993	n.d.	n.d.	n.d.	6.0	71.3	0.6	n.d.
E 48991	n.d.	107.5	142.6	110.5	71.9	22.5	15.2
E 48992	n.d.	n.d.	12.5	47.9	14.3	1.9	0.7

n.d.:not detected

P:phenanthrene, TMP:trimethylphenanthrene

Table A.21: (continued)

Sample	W-C_4-P $\frac{\mu g}{gTOC}$	X-C_4-P $\frac{\mu g}{gTOC}$	Y-C_4-P $\frac{\mu g}{gTOC}$	Z-C_4-P $\frac{\mu g}{gTOC}$	AA-C_4-P $\frac{\mu g}{gTOC}$	AB-C_4-P $\frac{\mu g}{gTOC}$	AC-C_4-P $\frac{\mu g}{gTOC}$
E 49710	13.2	n.d.	2.7	19.2	n.d.	7.0	2.9
E 48990	0.7	n.d.	1.0	n.d.	n.d.	n.d.	n.d.
E 48996	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48388	2.4	2.8	7.4	6.8	1.8	16.8	6.1
E 48389	1.1	0.8	4.1	9.3	1.2	10.3	3.3
E 48390	0.9	0.5	2.5	1.7	0.7	6.6	1.2
E 48214	1.0	1.1	2.9	5.9	1.1	7.4	2.6
E 48216	2.5	2.7	8.4	10.2	2.2	20.6	6.2
E 48403	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48220	2.5	2.3	6.8	2.2	2.7	15.7	4.4
E 48392	0.3	0.2	0.6	0.6	0.3	1.7	0.3
E 48393	0.4	0.6	1.3	1.0	0.4	2.1	1.7
E 48394	0.8	1.1	2.2	1.5	0.9	3.9	2.0
E 48395	0.2	0.4	0.5	0.1	0.2	1.3	0.3
E 48396	0.5	0.8	1.1	0.4	0.6	1.8	0.5
E 48397	0.4	0.9	1.3	0.3	0.3	2.2	0.8
E 48398	0.3	0.2	0.8	0.3	0.3	1.6	0.3
E 48400	1.1	0.4	2.2	n.d.	n.d.	5.3	1.1
E 48401	0.7	1.4	5.6	5.3	0.7	12.3	2.9
E 48405	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48382	0.2	1.0	0.7	0.4	0.2	1.6	0.7
E 48383	2.0	1.2	2.8	0.9	1.4	9.1	1.5
E 48384	0.1	0.2	0.4	0.1	n.d.	0.6	0.3
E 48985	n.d	91.0	n.d.	n.d.	n.d.	n.d.	70.6
E 48986	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48987	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48988	n.d.	n.d.	6.6	n.d.	n.d.	n.d.	5.2
E 48989	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	0.1
E 48993	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.8
E 48991	17.7	n.d.	36.1	n.d.	n.d.	n.d.	n.d.
E 48992	0.5	n.d.	1.8	n.d.	n.d.	n.d.	n.d.

n.d.:not detected
P:phenanthrene

Table A.21: (continued)

Sample	AD-C_4-P $\frac{\mu g}{gTOC}$	AE-C_4-P $\frac{\mu g}{gTOC}$	SUM $\frac{\mu g}{gTOC}$
E 49710	5.3	7.8	1118.0
E 48990	n.d.	0.9	282.8
E 48996	n.d.	n.d.	268.8
E 48388	4.2	7.9	1360.5
E 48389	2.2	3.8	790.0
E 48390	1.3	2.5	691.1
E 48214	2.0	3.1	935.8
E 48216	4.5	8.1	1331.5
E 48403	n.d.	n.d.	732.9
E 48220	3.2	6.5	1129.3
E 48392	0.5	0.8	378.1
E 48393	0.6	1.4	393.7
E 48394	1.5	2.5	658.0
E 48395	0.3	0.6	351.7
E 48396	0.6	1.4	406.7
E 48397	0.5	1.3	351.2
E 48398	0.3	1.1	294.5
E 48400	1.2	2.9	551.7
E 48401	2.3	6.4	1341.3
E 48405	n.d.	n.d.	864.7
E 48382	0.3	1.1	617.9
E 48383	1.7	4.1	1058.9
E 48384	0.1	0.3	145.8
E 48985	n.d.	53.7	41418.2
E 48986	n.d.	n.d.	71.1
E 48987	n.d.	n.d.	73.3
E 48988	n.d.	3.7	930.3
E 48989	n.d.	0.1	151.8
E 48993	n.d.	0.2	233.2
E 48991	n.d.	66.4	6160.2
E 48992	n.d.	3.9	1053.7

n.d.:not detected
P:phenanthrene

Table A.22: Distribution of Alkylphenanthrenes (samples without standard)

Sample	P	3-MP	2-MP	9-MP	1-MP	3-EP	2-EP
	%	%	%	%	%	%	%
E 48478	60.1	22.0	29.5	36.1	25.4	2.1	2.5
E 48479	100.0	25.4	32.3	51.9	34.6	2.5	4.9
E 49748	100.0	41.5	47.4	60.2	54.8	9.1	13.1
E 49749	38.3	22.2	30.9	37.3	34.5	4.3	4.9
E 49750	35.0	21.6	30.5	36.7	33.0	4.5	5.7
E 49751	100.0	39.2	40.5	58.8	50.5	2.9	5.6
E 48430	68.4	35.5	48.0	43.7	46.7	4.8	32.5
E 48425	100.0	76.2	110.6	13.8	12.2	2.6	12.2

P:phenanthrene, MP:methylphenanthrene
EP:ethylphenanthrene

Table A.22: (continued)

Sample	3,6-DMP	9-EP	2,6-DMP	2,7-DMP	1,3- + 2,10- + 3,9-3,10-DMP	1,6-2,9-DMP
	%	%	%	%	%	%
E 48478	7.6	1.9	7.3	5.7	39.0	20.5
E 48479	8.8	2.9	8.2	6.2	62.5	29.6
E 49748	15.1	12.3	7.4	6.1	39.9	11.1
E 49749	7.7	0.0	5.7	5.4	37.3	8.0
E 49750	6.7	0.0	6.0	5.7	37.0	7.5
E 49751	3.8	3.0	6.7	4.8	43.0	10.8
E 48430	3.4	4.0	4.1	9.1	8.0	11.4
E 48425	0.9	3.2	8.7	24.2	17.9	3.3

DMP:dimethylphenanthrene

Table A.22: (continued)

Sample	1,7-DMP %	2,3-DMP %	1,9- + 4,6-DMP %	1,8-DMP %	A-C_3-P %	B-C_3-P %	C-C_3-P %
E 48478	28.7	7.3	9.4	7.9	1.4	2.2	2.1
E 48479	32.5	8.2	16.2	10.1	1.0	3.8	3.1
E 49748	24.8	10.6	16.2	13.8	0.0	0.0	9.2
E 49749	27.4	8.9	12.4	10.3	0.0	3.1	7.0
E 49750	28.1	9.5	11.7	10.4	0.0	3.3	6.8
E 49751	20.6	7.3	0.0	9.5	0.0	0.0	3.6
E 48430	28.4	13.4	15.0	10.6	0.0	0.0	4.2
E 48425	4.6	6.8	0.0	0.0	0.0	0.0	1.2

DMP:dimethylphenanthrene, P:phenanthrene

Table A.22: (continued)

Sample	D-C_3-P %	E-C_3-P %	F-C_3-P %	G-C_3-P %	H-C_3-P %	I-C_3-P %	J-C_3-P %
E 48478	1.1	5.2	1.7	0.7	55.7	0.0	42.6
E 48479	1.8	9.3	3.1	0.0	52.7	0.0	61.3
E 49748	2.2	11.0	6.3	4.2	11.0	8.3	21.7
E 49749	1.9	7.9	4.4	1.3	10.3	6.2	26.6
E 49750	1.5	8.5	4.0	1.4	9.9	7.1	25.0
E 49751	0.8	6.5	1.9	0.0	9.5	0.0	19.3
E 48430	2.6	9.9	3.2	0.0	8.7	0.0	34.7
E 48425	1.2	2.3	0.5	0.0	3.7	0.0	0.0

P:phenanthrene

Table A.22: (continued)

Sample	K-C_3-P %	L-C_3-P %	M-C_3-P %	N-C_3-P %	O-C_3-P %	P-C_3-P %	Q-C_3-P %
E 48478	0.0	3.0	24.6	2.8	6.4	3.6	4.3
E 48479	0.0	6.2	37.9	4.4	9.5	6.4	7.1
E 49748	0.0	0.0	11.3	3.4	3.3	3.4	0.0
E 49749	0.0	2.2	13.7	3.2	3.0	3.5	0.0
E 49750	0.0	2.1	13.6	2.9	3.7	3.1	0.4
E 49751	0.0	2.6	12.4	1.7	2.6	2.9	0.0
E 48430	0.0	0.5	8.6	3.9	3.7	2.3	2.1
E 48425	0.0	1.6	0.0	2.6	0.2	0.0	0.0

P:phenanthrene

Table A.22: (continued)

Sample	R-C_3-P %	S-C_3-P %	T-C_3-P %	1,2,8-TMP %	Retene %	U-C_4-P %	V-C_4-P %
E 48478	7.3	2.9	9.2	100.0	6.0	1.1	0.0
E 48479	11.0	3.4	12.4	67.3	3.9	0.0	6.1
E 49748	0.0	2.6	9.8	22.3	16.9	2.2	0.0
E 49749	0.0	2.3	9.6	100.0	9.8	1.5	0.4
E 49750	0.0	2.4	9.3	100.0	10.2	2.1	8.0
E 49751	0.0	1.7	6.3	44.8	4.4	0.8	0.5
E 48430	0.0	6.4	21.3	23.4	100.0	1.8	0.0
E 48425	0.0	0.9	0.3	0.4	0.4	0.0	0.0

P:phenanthrene, TMP: trimethylphenanthrene

Table A.22: (continued)

Sample	W-C_4-P	X-C_4-P	Y-C_4-P	Z-C_4-P	AA-C_4-P	AB-C_4-P	AC-C_4-P
	%	%	%	%	%	%	%
E 48478	6.2	3.5	13.1	0.0	0.2	18.5	4.0
E 48479	0.0	0.0	21.2	0.0	0.0	25.4	8.4
E 49748	0.0	0.0	0.0	0.0	0.0	6.2	0.0
E 49749	0.0	0.0	2.8	2.9	0.0	7.1	0.9
E 49750	0.0	0.0	2.6	2.9	0.0	7.1	1.5
E 49751	1.2	0.0	2.4	0.0	0.0	4.3	1.7
E 48430	2.3	0.0	0.2	0.0	0.0	0.0	0.0
E 48425	0.0	0.0	0.0	0.0	0.0	0.0	0.0

P:phenanthrene

Table A.22: (continued)

Sample	AC-C_4-P	AD-C_4-P
	%	%
E 49748	0.0	4.4
E 49749	1.6	3.6
E 49750	1.4	3.7
E 49751	0.7	2.6
E 48478	0.0	11.6
E 48479	0.0	0.0
E 48425	0.0	0.0
E 48430	0.0	1.0

P:phenanthrene

Table A.23: Concentrations of Alkylbiphenyls

Sample	BP	2-MBP	DPM	3-MBP	4-MBP	1,1DPE
	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$
E 49710	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48990	0.1	>0.1	0.1	16.5	0.2	>0.1
E 48996	>0.1	>0.1	2.6	>0.1	1.0	>0.1
E 48388	12.5	1.2	6.8	9.7	0.5	6.0
E 48389	11.8	0.5	2.9	35.1	8.0	0.3
E 48390	12.5	0.5	2.6	41.3	8.1	0.3
E 48214	13.2	0.8	3.8	42.2	11.1	0.5
E 48216	11.6	0.8	2.7	39.1	8.6	0.4
E 48403	>0.1	0.2	0.5	18.7	0.4	>0.1
E 48220	1.1	0.8	2.7	39.1	8.6	0.4
E 48392	2.8	0.4	1.7	22.5	3.6	0.2
E 48393	1.7	0.3	1.3	26.2	3.0	0.2
E 48394	0.7	0.5	1.6	25.1	2.9	0.3
E 48395	7.3	0.5	1.6	41.6	5.5	0.4
E 48396	0.3	0.3	1.6	21.8	1.6	0.3
E 48397	>0.1	0.2	0.3	17.7	0.6	0.2
E 48398	0.9	0.4	1.7	24.1	2.0	0.2
E 48400	2.1	0.2	0.9	34.8	3.6	0.4
E 48401	0.5	>0.1	0.5	28.1	2.2	0.2
E 48405	47.5	0.5	1.5	110.5	23.0	0.1
E 48382	37.1	1.7	3.7	60.0	11.0	0.6
E 48383	10.6	1.0	7.2	41.6	9.0	0.8
E 48384	4.2	0.1	0.4	22.7	1.7	0.1
E 48985	53.4	n.d.	n.d.	449.5	219.8	n.d.
E 48986	0.8	>0.1	0.1	1.0	0.3	0.1
E 48987	0.3	>0.1	>0.1	0.5	0.2	>0.1
E 48988	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48989	10.4	>0.1	0.6	6.2	2.8	0.4
E 48993	0.2	>0.1	0.9	>0.1	>0.1	>0.1
E 48991	26.9	>0.1	13.6	66.8	28.3	1.2
E 48992	11.7	>0.1	>0.1	8.9	2.3	>0.1

n.d.:not detected
BP:biphenyl, MBP:methylbiphenyl
DPM:diphenylmethane, DPE:diphenylethane

Table A.23: (continued)

Sample	A-C_2 -BP $\frac{\mu g}{gTOC}$	B-C_2 -BP $\frac{\mu g}{gTOC}$	C-C_2 -BP $\frac{\mu g}{gTOC}$	D-C_2 -BP $\frac{\mu g}{gTOC}$	E-C_2 -BP $\frac{\mu g}{gTOC}$	F-C_2 -BP $\frac{\mu g}{gTOC}$	SUM $\frac{\mu g}{gTOC}$
E 49710	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48990	0.1	0.1	0.1	0.5	1.1	0.6	19.4
E 48996	>0.1	>0.1	1.4	0.2	1.5	>0.1	6.7
E 48388	6.0	1.9	2.2	3.3	6.7	13.2	105.8
E 48389	2.0	0.9	1.2	1.8	3.7	8.1	76.3
E 48390	1.7	0.6	1.4	1.8	5.2	8.1	85.0
E 48214	3.5	1.1	2.0	2.3	6.8	13.3	100.7
E 48216	3.8	1.1	1.8	3.3	>0.1	10.3	83.6
E 48403	1.0	0.5	1.5	3.5	14.6	10.4	51.3
E 48220	1.8	0.6	1.7	2.4	6.2	11.3	55.9
E 48392	1.3	0.4	1.2	0.8	2.1	3.0	40.8
E 48393	1.2	0.3	1.1	0.8	2.1	3.0	41.0
E 48394	1.6	0.4	1.7	1.3	3.1	5.6	76.8
E 48395	1.8	0.9	2.6	1.3	3.1	5.0	39.1
E 48396	1.1	0.4	2.6	0.9	3.1	5.0	39.1
E 48397	1.1	0.4	0.8	1.7	4.4	4.1	31.5
E 48398	1.0	0.5	1.1	1.7	3.4	4.3	41.3
E 48400	0.9	0.3	3.1	1.2	4.4	4.9	56.8
E 48401	1.0	0.3	1.7	1.2	4.7	>0.1	40.3
E 48405	1.3	0.4	2.8	5.5	13.1	14.8	220.8
E 48382	2.8	1.1	3.0	1.8	3.9	3.5	130.2
E 48383	3.8	1.6	2.0	2.8	7.1	8.4	95.7
E 48384	0.3	0.1	0.4	0.3	0.9	1.1	32.2
E 48985	n.d.	n.d.	37.3	218.1	379.0	326.5	1683.6
E 48986	0.1	>0.1	0.1	0.2	0.4	0.4	3.4
E 48987	>0.1	>0.1	>0.1	0.1	0.2	0.2	1.5
E 48988	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48989	0.3	0.3	0.7	0.7	1.9	1.8	26.1
E 48993	0.2	>0.1	>0.1	>0.1	>0.1	>0.1	1.1
E 48991	9.7	6.5	6.9	9.2	23.9	18.2	211.3
E 48992	>0.1	>0.1	1.0	0.3	1.2	>0.1	25.4

n.d.:not detected
BP:biphenyl

Table A.24: Concentrations of Alkylfluorenes

Sample	Fluorene $\frac{\mu g}{gTOC}$	3-MF $\frac{\mu g}{gTOC}$	2-MF $\frac{\mu g}{gTOC}$	1-MF $\frac{\mu g}{gTOC}$	4-MF $\frac{\mu g}{gTOC}$	SUM $\frac{\mu g}{gTOC}$
E 49710	1.5	6.0	4.6	16.2	4.8	33.1
E 48990	0.1	0.6	0.8	1.8	0.3	3.6
E 48996	0.7	2.9	3.0	6.2	1.9	14.7
E 48388	1.8	5.2	6.2	13.1	2.5	28.8
E 48389	1.2	2.9	4.6	8.1	1.2	18.0
E 48390	1.3	2.9	4.8	8.8	1.2	19.0
E 48214	2.1	4.5	6.8	12.4	2.0	27.8
E 48216	2.0	5.2	7.3	14.8	2.6	31.8
E 48403	2.1	5.7	7.5	20.3	1.9	37.5
E 48220	1.9	4.8	6.5	15.3	2.4	30.8
E 48392	1.0	1.8	2.4	7.4	0.8	13.5
E 48393	0.8	1.9	2.4	7.4	0.8	12.4
E 48394	1.2	2.6	3.1	11.2	1.3	19.4
E 48395	1.0	2.7	3.7	7.8	1.1	16.3
E 48396	1.4	2.3	2.5	8.2	1.1	15.4
E 48397	1.1	2.6	3.0	9.0	1.2	16.9
E 48398	1.9	2.4	2.9	9.0	0.9	17.1
E 48400	1.2	2.5	3.2	8.0	1.0	15.8
E 48401	1.9	3.7	5.3	18.4	1.7	31.0
E 48405	5.1	8.5	10.3	22.9	2.4	49.3
E 48382	2.7	3.7	3.6	11.7	1.5	23.1
E 48383	4.3	7.4	8.8	17.7	3.1	41.4
E 48384	0.3	0.5	0.5	1.7	0.2	3.1
E 48985	25.9	138.1	120.1	300.6	44.4	729.1
E 48986	>0.1	0.1	>0.1	0.1	>0.1	0.3
E 48987	>0.1	>0.1	>0.1	0.1	>0.1	0.1
E 48988	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48989	0.6	0.2	0.4	0.4	0.1	1.6
E 48993	0.8	2.9	3.0	6.2	1.9	14.7
E 48991	6.1	18.8	19.5	52.6	10.5	107.4
E 48992	0.4	1.4	0.9	6.7	1.3	10.7

n.d.:not detected
MF:methylfluorene

Table A.25: Concentration of Phenylnaphthalenes

Sample	2-PHN	A-C_1-PHN	$B-C_1$-PHN	$C-C_1$-PHN	D-C_1-PHN	E-C_1-PHN	SUM
	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$
E 49710	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48990	0.1	0.1	0.1	0.5	1.1	0.6	19.4
E 48996	>0.1	>0.1	1.4	0.2	1.5	>0.1	6.7
E 48388	19.8	2.8	8.3	8.7	2.3	2.4	44.3
E 48389	14.7	1.9	5.4	6.8	1.6	1.6	32.0
E 48390	16.1	2.0	6.0	7.0	1.5	1.7	34.3
E 48214	15.4	2.7	6.1	5.6	1.5	1.4	32.8
E 48216	18.0	3.6	8.7	8.3	2.1	2.4	43.2
E 48403	35.6	1.6	19.9	26.5	3.8	5.6	93.0
E 48220	22.9	7.1	11.5	14.4	2.7	4.1	62.7
E 48392	18.0	2.6	3.9	9.2	0.8	1.7	36.3
E 48393	16.1	2.4	3.4	8.3	0.8	1.7	32.7
E 48394	26.7	3.9	6.6	12.6	1.5	3.1	54.3
E 48395	16.4	2.0	4.6	6.7	1.1	1.8	32.5
E 48396	11.8	0.9	4.0	4.9	0.8	1.6	23.9
E 48397	9.6	0.8	4.0	4.4	0.9	1.4	21.0
E 48398	15.1	0.5	4.5	5.5	1.1	1.6	28.4
E 48400	21.6	1.8	8.4	14.0	1.5	3.1	50.4
E 48401	36.5	5.4	17.2	20.0	3.4	6.3	88.8
E 48405	56.5	1.2	17.2	24.3	3.0	4.5	106.6
E 48382	44.1	4.7	7.7	11.2	1.9	3.6	73.2
E 48383	24.3	3.2	8.9	7.8	2.0	2.5	48.6
E 48384	3.7	0.2	1.3	1.1	0.3	0.4	7.1
E 48985	1490.7	47.3	557.8	411.0	40.3	62.2	2609.3
E 48986	1.7	>0.1	10.1	0.1	>0.1	>0.1	12.0
E 48987	2.2	>0.1	0.2	0.2	>0.1	0.1	2.8
E 48988	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48989	3.2	>0.1	12.9	0.2	0.1	0.1	16.5
E 48993	3.0	0.4	15.9	0.7	0.3	0.3	20.7
E 48991	140.8	10.2	54.3	46.2	17.9	21.0	290.4
E 48992	23.9	1.1	6.2	4.5	2.6	2.6	40.9

n.d.:not detected
PHN:phenylnaphthalene

Table A.26: Distribution of Alkylbiphenyls (samples without standard)

Compound	BP	2-MBP	DPM	3-MBP	4-MBP	1,1DPE
	%	%	%	%	%	%
E 48478	10.7	1.6	9.7	100.0	17.5	0.0
E 49748	98.0	0.0	0.0	100.0	27.2	8.6
E 49751	44.5	9.1	0.0	100.0	19.9	0.0

BP:biphenyl, DPM:diphenylmethane
MBP:methylbiphenyl, MF:Diphenylethane

Table A.26: (continued)

Compound	$A-C_2$ -BP	B-C_2 -BP	C-C_2 -BP	D-C_2 -BP	E-C_2 -BP	F-C_2 -BP
	%	%	%	%	%	%
E 48478	7.0	0.0	7.2	14.8	26.9	22.8
E 49748	20.8	0.0	21.2	10.6	23.5	24.4
E 49751	0.0	0.0	8.4	13.2	20.8	0.0

BP:biphenyl

Table A.27: Distribution of Alkylfluorenes (samples without standard)

Compound	Fluorene %	3-MF %	2-MF %	1-MF %	4-MF %
E 48478	12.1	22.5	19.3	100.0	12.6
E 48479	17.4	20.4	41.4	100.0	17.8
E 49751	7.7	30.1	34.0	100.0	43.1
E 48430	8.8	27.9	42.7	100.0	19.7
E 48425	4.2	28.0	23.9	100.0	5.6

MF:methylfluorene

Table A.28: Distribution of Phenylnaphthalenes (samples without standard)

Compound	1-PHN	2-PHN	A-C_1-PHN	B-C_1-PHN	C-C_1-PHN	D-C_1-PHN	E-C_1-PHN
E 49748	100.0	32.5	2.9	8.6	6.0	4.1	1.1
E 49749	100.0	24.8	1.6	9.4	6.6	3.1	3.5
E 49750	100.0	26.4	1.8	9.8	7.8	3.5	3.6
E 49751	100.0	110.9	2.6	34.9	31.7	15.3	17.7
E 48478	100.0	21.1	2.9	9.0	8.8	2.7	3.0
E 48479	100.0	22.5	3.6	11.0	11.0	3.7	4.5
E 48430	43.4	100.0	15.9	38.0	33.9	12.5	12.3
E 48425	18.5	100.0	1.2	41.4	45.7	2.3	3.2

PHN:phenylnaphthalene

A.4 NSO-Compounds

Table A.29: Concentrations of Alkyldibenzothiophenes

Sample	DBT	4-M DBT	2-M DBT	3-M DBT	1-M DBT	4-E DBT	4,6-DM DBT	SUM
	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$
E 49710	14.3	16.6	7.3	7.3	17.9	1.1	1.5	66.1
E 48990	0.7	3.1	1.0	0.8	0.3	0.1	0.3	6.2
E 48996	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48388	11.2	11.7	6.4	5.8	6.6	0.8	2.7	45.2
E 48389	5.8	5.3	3.3	2.7	1.7	0.3	0.9	20.0
E 48390	5.4	4.7	2.3	2.6	1.8	0.3	0.7	17.9
E 48214	9.6	8.1	4.3	4.9	2.7	0.5	1.3	31.3
E 48216	7.9	8.9	5.5	4.1	8.4	0.6	2.0	32.4
E 48403	6.8	19.8	5.6	5.3	1.0	0.6	5.1	44.2
E 48220	4.9	7.7	4.1	3.4	2.7	0.5	1.6	25.0
E 48392	3.6	2.8	1.3	1.4	1.7	0.2	0.4	11.4
E 48393	3.1	2.5	1.3	1.1	1.3	0.1	0.5	9.9
E 48394	4.5	4.0	1.9	2.0	2.1	0.3	0.7	15.6
E 48395	3.4	3.0	1.6	1.5	1.5	0.2	0.4	11.6
E 48396	2.9	2.6	1.4	1.3	1.8	0.2	0.4	10.7
E 48397	3.7	3.5	1.8	1.8	2.0	0.3	0.6	13.7
E 48398	10.8	5.3	2.8	1.8	2.1	0.3	0.6	23.7
E 48400	2.6	2.7	1.7	1.6	1.8	0.2	0.5	11.2
E 48401	6.4	10.4	4.4	4.6	4.0	0.6	3.0	33.4
E 48405	11.7	19.5	3.8	6.1	0.9	0.5	3.7	46.3
E 48382	7.2	4.0	3.5	1.9	1.9	0.3	0.8	19.7
E 48383	10.6	8.5	6.9	4.2	8.0	0.5	1.2	35.0
E 48384	1.2	1.3	0.5	0.5	0.5	0.1	0.3	4.4
E 48985	1110	2244	641	986	206	75	768	6033
E 48986	1.6	0.2	0.1	0.2	0.0	0.0	0.2	2.3
E 48987	0.8	0.5	0.1	0.1	0.1	0.0	0.2	1.8
E 48988	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48989	4.0	1.3	0.3	0.4	0.2	0.1	0.4	6.6
E 48993	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48991	27.1	26.2	15.7	17.0	6.0	2.7	5.2	100.0
E 48992	5.8	4.4	1.5	2.6	4.9	0.0	0.0	19.2

n.d.: not detected
DBT:dibenzothiophene

Table A.30: Distribution of Alkyldibenzothiophenes (samples without standard)

Sample	-DBT	4-M -DBT	2-M -DBT	3-M -DBT	1-M -DBT	4-E -DBT	4,6-DM -DBT
	%	%	%	%	%	%	%
E 49748	100.0	88.9	38.8	33.3	26.5	10.7	34.0
E 49749	23.5	49.0	16.0	18.5	100.0	5.1	28.7
E 49750	22.1	51.7	17.1	18.9	100.0	6.1	31.7
E 49751	76.9	80.9	19.6	25.9	100.0	5.5	23.9
E 48430	72.5	100.0	46.3	59.3	0.0	12.6	43.5
E 48425	49.4	100.0	29.0	35.5	0.0	1.7	26.9

MDBT:methyldibenzothiophene
DMDBT:dimethyldibenzothiophene

Table A.31: Concentrations of Alkyldibenzofurans

Sample	DBF	4-MDBF	2-MDBF	3-MDBF	1-MDBF
	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$
E 49710	41.78	44.24	54.37	25.31	27.87
E 48990	0.29	2.66	1.71	0.50	1.95
E 48996	3.88	41.91	12.92	5.47	7.92
E 48388	91.74	67.11	133.75	51.18	44.50
E 48389	55.81	42.10	59.54	25.13	23.26
E 48390	47.52	35.59	50.30	29.25	23.02
E 48214	57.25	53.44	77.61	33.06	31.28
E 48216	50.49	50.15	70.67	36.21	29.59
E 48403	1.17	11.69	5.02	11.83	7.07
E 48220	14.54	32.96	43.43	24.53	21.47
E 48392	26.75	25.94	25.23	12.88	10.65
E 48393	20.50	23.87	21.49	11.27	9.31
E 48394	28.85	36.82	33.31	15.46	14.77
E 48395	14.10	18.38	13.97	9.43	10.41
E 48396	5.78	17.43	6.18	8.88	6.48
E 48397	0.29	6.83	3.17	5.53	2.90
E 48398	3.17	13.74	8.95	7.80	8.72
E 48400	8.32	21.83	19.89	8.69	10.39
E 48401	6.97	29.73	21.40	14.65	17.93
E 48405	5.05	16.81	4.68	5.49	12.41
E 48382	48.99	37.51	23.26	16.13	16.65
E 48383	36.91	60.01	49.06	37.55	32.74
E 48384	4.72	5.48	2.99	2.65	2.62
E 48985	415.02	353.83	238.28	133.33	155.67
E 48986	5.75	2.31	2.28	1.27	0.71
E 48987	4.12	1.20	1.24	0.69	0.36
E 48988	4.81	27.26	7.14	1.66	3.46
E 48989	35.95	8.57	8.23	5.09	2.49
E 48993	5.31	6.03	11.38	3.32	8.07
E 48991	203.45	216.75	260.84	121.08	111.85
E 48992	20.89	24.39	22.87	10.63	11.70

DBF:dibenzofuran, MDBF:methyldibenzofuran

Table A.31: (continued)

Sample	DMDBF1 $\frac{\mu g}{gTOC}$	EDBF2 $\frac{\mu g}{gTOC}$	DMDBF3 $\frac{\mu g}{gTOC}$	DMDBF4 $\frac{\mu g}{gTOC}$	DMDBF5 $\frac{\mu g}{gTOC}$
E 49710	35.19	28.65	23.45	26.73	11.06
E 48990	4.84	0.00	3.98	2.00	2.16
E 48996	30.79	0.00	15.91	9.60	8.04
E 48388	31.90	35.28	32.88	8.77	17.67
E 48389	16.04	13.55	14.72	4.64	11.58
E 48390	13.19	12.71	15.70	5.47	8.59
E 48214	22.12	22.85	21.56	6.51	12.15
E 48216	29.36	21.49	24.33	7.15	16.17
E 48403	7.07	1.25	12.68	5.76	8.16
E 48220	22.03	19.43	18.95	7.15	12.23
E 48392	7.38	13.79	7.83	1.85	3.37
E 48393	6.88	12.01	8.21	2.33	3.83
E 48394	13.26	20.94	12.46	2.49	6.46
E 48395	4.83	8.30	3.92	1.76	3.75
E 48396	6.23	8.79	7.91	1.46	3.52
E 48397	5.23	4.68	7.27	1.89	3.26
E 48398	4.57	7.27	6.17	1.24	4.04
E 48400	8.96	11.98	11.08	3.15	5.87
E 48401	16.89	16.54	21.81	4.84	11.19
E 48405	3.77	1.03	6.94	2.05	5.21
E 48382	5.58	10.47	7.36	2.26	2.74
E 48383	24.11	17.57	24.63	9.29	8.81
E 48384	1.22	1.16	1.64	0.44	0.59
E 48985	288.11	0.00	293.62	191.62	179.98
E 48986	1.26	0.00	1.14	0.76	0.38
E 48987	0.57	0.00	0.57	0.37	0.17
E 48988	19.09	0.00	10.69	4.69	3.64
E 48989	3.37	0.00	2.98	2.00	0.95
E 48993	13.67	0.00	8.64	4.51	4.55
E 48991	196.19	0.00	95.51	83.25	62.73
E 48992	14.48	16.50	10.62	5.59	4.18

DMDBF:dimethyldibenzofuran, EDBF:ethyldibenzofuran

Table A.31: (continued)

Sample	DMDBF6 $\frac{\mu g}{gTOC}$	EDBF7 $\frac{\mu g}{gTOC}$	DMDBF8 $\frac{\mu g}{gTOC}$	DMDBF9 $\frac{\mu g}{gTOC}$	DMDBF10 $\frac{\mu g}{gTOC}$
E 49710	9.53	10.28	71.10	11.44	0.14
E 48990	1.95	0.00	7.97	1.25	33.71
E 48996	14.26	0.00	26.90	9.63	0.01
E 48388	8.98	6.93	91.06	10.97	12.29
E 48389	4.97	3.14	41.93	6.74	1.65
E 48390	5.93	2.65	42.43	6.30	5.84
E 48214	6.35	4.81	40.47	8.32	15.21
E 48216	7.88	6.41	40.66	9.52	11.05
E 48403	11.17	1.35	19.12	4.65	0.98
E 48220	9.39	5.16	32.28	8.22	1.58
E 48392	2.69	1.65	16.29	2.31	3.80
E 48393	2.27	2.01	9.02	1.15	1.80
E 48394	4.04	4.00	23.81	3.71	0.80
E 48395	2.33	1.23	6.24	1.84	7.64
E 48396	2.19	3.02	13.36	2.46	2.07
E 48397	2.17	2.33	10.38	1.76	1.67
E 48398	2.08	1.56	8.59	2.12	11.34
E 48400	3.14	3.18	15.74	3.66	0.42
E 48401	6.49	5.89	38.09	6.67	18.58
E 48405	7.37	0.00	13.52	3.21	6.11
E 48382	2.83	1.05	5.53	2.85	8.38
E 48383	9.68	6.47	51.69	8.90	0.68
E 48384	0.75	0.22	2.50	0.47	9.05
E 48985	245.52	0.00	633.81	1141.15	322.65
E 48986	0.46	0.00	1.95	0.35	0.08
E 48987	0.21	0.00	1.05	0.14	0.00
E 48988	8.74	0.00	24.30	6.75	362.62
E 48989	1.05	0.00	4.76	0.77	6.46
E 48993	7.39	0.00	19.49	2.38	0.01
E 48991	66.71	0.00	247.5	49.80	1.18
E 48992	7.99	0.00	27.11	3.55	1745.79

DMDBF:dimethyldibenzofuran, EDBF:ethyldibenzofuran

Table A.31: (continued)

Sample	DMDBF11 $\frac{\mu g}{gTOC}$	SUM $\frac{\mu g}{gTOC}$
E 49710	16.89	435.57
E 48990	1.00	65.98
E 48996	3.83	191.09
E 48388	13.46	658.49
E 48389	6.84	331.63
E 48390	7.36	311.82
E 48214	11.44	424.43
E 48216	13.53	424.65
E 48403	2.02	108.98
E 48220	11.04	284.39
E 48392	3.61	166.00
E 48393	4.36	140.30
E 48394	6.96	228.14
E 48395	2.54	110.68
E 48396	4.58	100.34
E 48397	3.05	62.38
E 48398	3.17	94.51
E 48400	5.67	141.98
E 48401	7.18	244.85
E 48405	1.41	95.06
E 48382	3.07	194.67
E 48383	13.32	391.42
E 48384	0.45	36.95
E 48985	164.18	4756.78
E 48986	0.19	18.89
E 48987	0.10	10.77
E 48988	0.00	484.84
E 48989	0.56	83.19
E 48993	4.55	99.30
E 48991	43.14	1759.99
E 48992	3.52	1929.81

DMDBF:dimethyldibenzofuran

Table A.32: Concentrations of Benzo[*b*]naphthofurans

Sample	2,1-BNF	1,2-BNF	2,3-BNF	BNF	SUM
	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$	$\frac{\mu g}{gTOC}$
E 49710	33.38	28.18	18.33	11.10	91.00
E 48990	0.99	5.90	0.33	2.68	9.91
E 48996	8.25	13.40	7.09	8.61	37.36
E 48388	19.21	25.59	5.43	6.19	56.43
E 48389	13.07	17.41	3.74	4.94	39.16
E 48390	8.91	12.89	2.17	3.22	27.19
E 48214	12.74	15.63	4.77	3.90	37.04
E 48216	18.88	18.62	3.80	5.56	46.86
E 48403	0.72	2.56	0.79	2.06	6.13
E 48220	17.17	21.96	3.65	5.09	47.88
E 48392	5.48	6.51	1.57	2.22	15.79
E 48393	4.56	6.66	2.01	2.03	15.26
E 48394	9.10	11.97	3.23	3.62	27.92
E 48395	4.78	6.66	0.92	2.25	14.62
E 48396	4.53	5.82	1.37	2.51	14.22
E 48397	3.45	6.20	0.31	1.62	11.57
E 48398	3.36	5.98	0.54	1.94	11.81
E 48400	6.29	11.21	0.80	2.82	21.12
E 48401	13.58	22.36	2.69	7.10	45.73
E 48405	0.43	2.56	0.57	1.46	5.02
E 48382	15.52	16.78	4.16	9.48	45.94
E 48383	19.86	20.79	4.60	7.95	53.21
E 48384	0.87	1.87	0.18	0.61	3.53
E 48985	240.73	208.63	110.16	199.49	759.01
E 48986	1.03	0.38	0.27	0.24	1.92
E 48987	1.84	0.70	0.49	0.29	3.32
E 48988	12.70	24.81	6.52	11.47	55.50
E 48989	1.57	0.66	0.46	0.32	3.02
E 48993	12.37	15.98	11.78	5.69	45.82
E 48991	141.22	154.71	36.50	41.35	373.78
E 48992	18.26	21.29	1.44	4.19	45.18

BNF:benzo[*b*]naphthofuran

Table A.33: Distribution of Alkyldibenzofurans (samples without standard)

Sample	DBF	4-MDBF	2-MDBF	3-MDBF	1-MDBF
	%	%	%	%	%
E 48478	59.0	89.9	61.8	46.4	43.2
E 48479	100.0	62.7	45.6	29.8	32.6
E 49748	37.1	34.9	43.5	18.5	48.6
E 49749	0.6	0.2	0.5	0.2	0.2
E 49750	4.3	2.0	3.6	1.7	2.1
E 49751	39.0	53.4	72.0	17.2	43.4
E 48430	55.8	85.7	100.0	30.2	47.6
E 48425	0.4	2.9	0.8	0.7	2.1

DBF:dibenzofuran, MDBF:methyldibenzofuran

Table A.33: (continued)

Sample	DMDBF1	EDBF2	DMDBF3	DMDBF4	DMDBF5
	%	%	%	%	%
E 48478	38.3	33.7	56.3	19.5	23.6
E 48479	21.4	11.7	42.8	7.8	17.9
E 49748	30.8	26.9	3.1	14.6	13.6
E 49749	0.6	0.4	0.6	0.3	0.2
E 49750	10.7	7.0	10.3	6.3	4.3
E 49751	35.0	11.0	38.2	13.4	9.6
E 48430	86.5	0.0	39.1	33.4	15.9
E 48425	1.6	0.0	2.4	1.6	2.0

DMDBF:dimethyldibenzofuran, EDBF:ethyldibenzofuran

Table A.33: (continued)

Sample	DMDBF6 %	EDBF7 %	DMDBF8 %	DMDBF9 %	DMDBF10 %
E 48478	26.1	12.4	100.0	13.1	40.3
E 48479	16.3	15.6	66.8	6.6	0.0
E 49748	16.8	10.3	100.0	13.9	7.6
E 49749	0.2	0.1	2.3	0.4	100.0
E 49750	5.0	2.5	100.0	7.5	4.8
E 49751	16.4	1.7	100.0	9.1	0.4
E 48430	19.6	0.0	94.1	16.0	1.6
E 48425	2.9	0.0	3.5	1.5	100.0

DMDBF:dimethyldibenzofuran, EDBF:ethyldibenzofuran

Table A.33: (continued)

Sample	DMDBF11 %
E 48478	16.5
E 48479	25.0
E 49748	12.4
E 49749	0.3
E 49750	5.8
E 49751	6.6
E 48430	13.5
E 48425	0.3

DMDBF:dimethyldibenzofuran

Table A.34: Distribution of Benzo[*b*]naphthofurans(samples without standard)

Sample	2,1-BNF %	1,2-BNF %	2,3-BNF %	BNF %
E 48478	40.3	82.7	9.7	16.7
E 48479	17.0	41.9	21.9	9.8
E 49748	40.1	37.9	19.4	25.8
E 49749	4.6	5.7	2.1	1.8
E 49750	78.9	100.0	35.6	28.6
E 49751	9.8	17.7	5.1	8.0
E 48430	37.9	35.5	24.0	0.0
E 48425	0.0	0.0	0.0	0.0

BNF:benzo[*b*]naphthofuran

Table A.35: Distribution of Alkylcarbazoles

Sample	C	1-MC	3-MC	2-MC	4-MC
	%	%	%	%	%
E 49710	90.6	100.0	73.2	51.7	42.3
E 49748	84.7	100.0	8.9	69.5	131.2
E 49749	103.1	100.0	59.3	73.0	75.3
E 49450	159.2	100.0	78.7	110.7	116.6
E 48990	10.3	87.9	26.3	24.8	31.2
E 48996	30.8	38.6	18.4	24.2	41.8
E 48388	16.1	98.2	9.3	26.3	45.7
E 48389	22.8	100.0	17.7	20.6	28.9
E 48390	19.6	100.0	17.5	18.4	24.8
E 48214	16.9	100.0	14.3	16.9	21.0
E 48216	23.7	100.0	31.7	38.4	50.3
E 48403	9.5	100.0	66.2	45.2	90.9
E 48220	27.3	100.0	28.4	36.5	39.0
E 48392	27.3	100.0	11.3	13.8	19.3
E 48393	27.1	100.0	27.2	30.8	25.8
E 48394	31.3	100.0	25.0	28.8	28.8
E 48395	40.4	100.0	20.9	26.2	31.8
E 48397	25.1	100.0	18.3	23.5	24.0
E 48398	15.3	100.0	7.2	11.8	18.0
E 48400	34.9	100.0	15.3	19.4	35.0
E 48401	51.0	100.0	24.5	28.1	46.4
E 48405	70.1	100.0	37.7	28.1	43.0
E 48425	39.1	90.8	20.8	72.3	97.6
E 48382	81.4	100.0	35.7	26.9	41.7
E 48383	19.6	100.0	14.5	22.7	20.5
E 48384	49.8	100.0	34.7	29.5	38.2
E 48988	61.2	72.3	7.8	66.6	100.0
E 48991	21.4	65.6	19.0	29.6	44.2
E 48992	45.7	100.0	44.6	55.5	57.7

C:carbazole, MC:methylcarbazole

Table A.35: (continued)

Sample	1,8DMC	1,3-DMC	1,6-DMC	1,7-DMC	1,4-DMC
	%	%	%	%	%
E 49710	30.0	62.2	60.7	40.3	46.3
E 49748	38.2	46.5	43.7	37.8	63.6
E 49749	30.6	42.7	39.6	43.5	53.1
E 49450	32.8	61.6	57.1	55.0	96.2
E 48990	71.9	73.9	70.9	54.6	53.6
E 48996	29.8	42.7	46.0	72.9	55.9
E 48388	50.4	44.3	51.7	56.0	57.9
E 48389	34.3	34.9	39.4	57.2	47.4
E 48390	41.6	35.9	33.5	49.3	41.8
E 48214	49.9	34.3	35.3	47.4	43.0
E 48216	45.6	39.6	36.1	52.3	47.3
E 48403	62.1	83.2	46.5	69.9	70.6
E 48220	52.8	61.7	54.3	73.4	56.7
E 48392	44.4	31.9	31.6	46.0	26.5
E 48393	50.0	42.8	43.1	54.7	37.2
E 48394	46.6	47.3	46.2	57.1	42.4
E 48395	26.5	26.0	18.9	29.3	23.1
E 48397	48.8	48.5	45.0	60.5	42.3
E 48398	40.0	54.3	40.2	35.9	41.5
E 48400	39.4	42.9	34.5	40.8	41.3
E 48401	38.6	38.2	34.0	51.0	41.4
E 48405	22.4	22.8	16.8	20.0	24.5
E 48425	4.6	12.8	16.8	46.4	42.7
E 48382	13.0	21.7	17.7	13.9	18.5
E 48383	31.6	26.9	32.2	30.2	24.6
E 48384	23.7	24.4	20.6	27.5	28.6
E 48988	0	34.2	32.0	32.6	50.7
E 48991	31.4	40.8	35.0	61.1	48.0
E 48992	38.7	66.7	55.5	71.2	55.1

DMC:dimethylcarbazole

Table A.35: (continued)

Sample	1,5-DMC	2,6-DMC	2,7-DMC	1,2-DMC	2,4-DMC
	%	%	%	%	%
E 49710	32.6	28.1	39.7	22.3	25.1
E 49748	52.7	10.7	65.5	54.0	5.6
E 49749	38.3	30.8	44.8	32.2	42.0
E 49450	47.9	6.4	65.5	78.9	83.2
E 48990	69.8	13.5	38.7	12.0	18.1
E 48996	62.3	4.0	25.8	18.3	36.3
E 48388	52.5	2.3	22.9	6.3	8.6
E 48389	84.1	3.5	28.6	6.3	28.9
E 48390	59.1	2.9	19.1	3.7	10.8
E 48214	59.7	2.9	19.3	3.7	13.1
E 48216	63.7	5.4	31.3	9.8	26.4
E 48403	72.5	7.0	34.9	17.2	14.3
E 48220	73.0	8.6	37.6	10.0	27.1
E 48392	41.3	3.1	18.4	2.7	10.9
E 48393	52.8	6.0	28.2	7.0	18.4
E 48394	55.1	4.5	25.2	7.6	19.3
E 48395	30.9	2.5	14.5	4.6	7.7
E 48397	49.6	4.3	25.3	4.5	11.8
E 48398	33.7	10.3	20.4	9.6	11.2
E 48400	65.0	1.9	15.8	8.0	15.2
E 48401	53.1	2.7	27.2	7.5	14.5
E 48405	23.6	2.7	11.4	7.5	6.7
E 48425	100.0	6.9	61.1	19.1	67.8
E 48382	21.9	2.3	6.9	10.7	0.6
E 48383	27.9	1.7	11.5	2.8	6.3
E 48384	23.5	2.4	18.8	4.7	7.6
E 48988	38.8	7.1	43.6	41.3	53.6
E 48991	52.5	5.7	27.1	7.3	15.3
E 48992	44.3	9.7	47.4	12.4	38.0

DMC:dimethylcarbazole

Table A.35: (continued)

Sample	2,5-DMC	C_3-C	C_3-C	C_3-C	C_3-C
	%	%	%	%	%
E 49710	16.8	33.7	41.3	19.9	27.5
E 49748	71.1	40.0	94.9	25.9	58.5
E 49749	37.6	24.7	72.3	1.4	18.9
E 49450	75.1	23.7	161.1	16.9	0.0
E 48990	27.9	116.7	92.6	28.2	44.8
E 48996	21.9	50.5	100.0	17.5	21.3
E 48388	20.2	66.7	100.0	24.9	16.8
E 48389	30.5	40.4	73.9	17.9	86.8
E 48390	15.4	32.0	49.9	11.3	16.6
E 48214	12.8	35.5	54.6	11.7	29.7
E 48216	36.4	59.6	66.9	15.2	32.1
E 48403	30.6	63.7	68.0	15.9	29.8
E 48220	32.3	65.8	82.6	21.7	44.4
E 48392	11.5	33.9	39.8	10.1	17.5
E 48393	17.2	54.1	58.9	17.0	29.5
E 48394	19.2	51.7	58.7	16.2	32.2
E 48395	9.5	13.1	16.5	4.1	6.7
E 48397	10.6	61.1	59.1	18.8	23.4
E 48398	6.7	37.1	38.0	18.6	14.5
E 48400	14.2	33.7	43.8	9.3	17.4
E 48401	15.7	37.4	47.4	12.4	15.5
E 48405	7.5	0.0	0.0	0.0	0.0
E 48425	65.9	0.0	0.0	7.6	4.8
E 48382	7.4	4.3	0.0	0.0	0.0
E 48383	3.7	18.6	19.5	6.3	7.4
E 48384	6.8	14.6	18.9	4.6	6.4
E 48988	26.9	32.5	0.0	0.0	0.0
E 48991	26.6	56.3	100.0	23.8	18.6
E 48992	20.8	83.2	81.9	35.1	40.6

DMC:dimethylcarbazole, C:carbazole

Table A.35: (continued)

Sample	C_3-C %	C_3-C %	C_3-C %	C_3-C %	C_3-C %
E 49710	23.9	36.7	23.1	28.9	34.1
E 49748	185.0	198.3	56.4	93.1	56.3
E 49749	26.9	60.4	37.3	54.5	43.2
E 49450	0.0	0.0	0.0	0.0	0.0
E 48990	44.2	72.2	38.5	49.4	49.9
E 48996	41.6	5.3	46.5	67.1	47.9
E 48388	30.7	44.2	37.5	43.5	22.2
E 48389	31.1	45.9	51.8	50.2	35.9
E 48390	20.2	26.6	25.8	29.5	14.8
E 48214	19.0	27.9	27.7	32.7	11.2
E 48216	27.7	43.8	44.1	50.0	33.4
E 48403	30.8	48.2	24.3	38.9	27.0
E 48220	45.0	52.4	53.5	54.2	40.7
E 48392	17.8	23.0	20.8	20.4	16.8
E 48393	33.8	39.9	38.5	38.5	33.5
E 48394	31.8	36.2	34.4	36.6	29.4
E 48395	7.1	7.1	6.4	7.2	6.3
E 48397	32.1	41.3	29.1	38.9	24.5
E 48398	19.1	26.9	18.8	24.0	14.8
E 48400	15.1	40.7	26.4	41.3	13.9
E 48401	22.3	29.1	27.4	32.9	18.2
E 48405	0.0	0.0	0.0	0.0	0.0
E 48425	12.8	16.9	28.9	21.5	15.6
E 48382	0.0	0.0	0.0	0.0	0.0
E 48383	9.0	14.3	9.4	11.5	6.1
E 48384	10.0	15.7	7.9	10.7	7.7
E 48988	0.0	0.0	0.0	0.0	0.0
E 48991	30.7	37.5	29.0	54.5	33.2
E 48992	59.0	56.5	39.0	78.1	27.5

C:carbazole

Table A.35: (continued)

Sample	C_3-C %	C_3-C %	C_3-C %	C_3-C %
E 49710	4.8	9.6	9.5	5.6
E 49748	8.3	6.9	81.7	61.4
E 49749	11.1	14.2	27.7	12.1
E 49450	0.0	0.0	0.0	0.0
E 48990	7.9	33.8	16.9	11.0
E 48996	14.7	32.8	15.7	5.2
E 48388	11.7	13.5	14.7	11.9
E 48389	11.3	21.9	9.4	14.1
E 48390	5.7	9.3	3.6	7.6
E 48214	4.6	7.8	12.8	12.8
E 48216	9.3	19.9	20.4	13.9
E 48403	18.8	19.4	17.2	17.1
E 48220	14.4	19.6	17.6	16.6
E 48392	0.0	0.0	0.0	0.0
E 48393	11.5	14.9	11.8	12.7
E 48394	8.4	12.2	12.4	11.6
E 48395	0.0	0.0	0.0	0.0
E 48397	10.2	15.6	7.5	12.3
E 48398	7.8	8.4	5.1	8.4
E 48400	5.6	11.9	28.2	24.7
E 48401	6.8	10.5	17.3	17.3
E 48405	0.0	0.0	0.0	0.0
E 48425	6.2	0.0	0.0	0.0
E 48382	0.0	0.0	0.0	0.0
E 48383	3.2	4.7	3.7	0.0
E 48384	0.0	0.0	0.0	0.0
E 48988	0.0	0.0	0.0	0.0
E 48991	11.4	10.5	12.4	12.0
E 48992	33.2	23.1	26.4	29.6

C:carbazole

Table A.36: Distribution of Alkylfluoren-9-ones

Sample	F	1-MF	2-MF	3-MF	4-MF	1-EF
	%	%	%	%	%	%
E 49710	51.6	15.5	5.1	6.8	4.2	14.4
E 49748	24.5	21.6	29.9	2.8	6.6	4.8
E 49749	36.7	28.8	29.3	5.7	9.2	10.1
E 49750	66.2	32.0	5.2	6.8	6.0	9.5
E 49751	53.2	41.7	6.3	8.6	7.9	5.8
E 48990	15.9	12.7	3.5	2.1	0.4	n.d.
E 48478	55.3	21.8	12.9	10.4	11.3	7.9
E 47479	40.6	10.5	8.5	5.7	6.8	n.d.
E 48996	28.1	15.2	7.7	9.2	3.2	7.9
E 48388	62.8	32.6	14.8	12.9	5.7	12.4
E 48389	100.0	26.7	10.2	6.8	3.2	1.0
E 48390	100.0	31.1	12.4	7.3	4.5	6.6
E 48214	100.0	30.1	15.9	8.6	5.1	8.3
E 48216	100.0	43.6	27.8	14.1	7.4	12.3
E 48403	96.7	43.1	20.3	22.0	11.3	11.5
E 48220	71.6	34.1	9.7	12.7	6.5	10.4
E 48430	60.1	36.3	9.8	8.4	5.3	8.3
E 48392	100.0	55.3	16.3	2.7	4.8	10.9
E 48393	99.7	59.1	14.4	9.1	5.7	10.8
E 48394	68.6	38.2	17.6	7.6	5.6	10.3
E 48395	100.0	33.1	10.5	9.6	8.6	12.8
E 48396	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48397	100.0	33.1	10.5	9.6	8.6	12.8
E 48398	77.5	27.7	12.2	10.4	5.3	10.6
E 48400	100.0	37.0	11.4	9.8	6.8	15.4
E 48401	100.0	40.4	10.5	7.2	4.7	9.1
E 48405	100.0	18.0	7.3	6.8	2.9	3.9
E 48425	100.0	29.3	16.4	17.7	2.2	n.d.
E 48382	100.0	34.1	9.7	12.7	6.5	10.4
E 48383	100.0	19.3	6.4	5.0	2.7	4.3
E 48384	100.0	23.9	5.6	4.0	2.5	4.2
E 48985	78.0	10.3	2.4	10.7	2.7	n.d.
E 48986	100.0	6.4	3.4	3.6	2.8	1.5
E 48987	100.0	6.2	3.6	2.7	1.8	1.3
E 48988	19.8	21.6	27.0	4.9	4.8	6.5
E 48989	100.0	2.8	1.9	1.6	1.4	1.1
E 48993	39.0	5.3	100.0	95.9	4.3	8.4
E 48991	82.5	23.9	6.5	4.4	2.9	2.9
E 48992	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.:not detected
F:fluoren-9-one, MF:methylfluoren-9-one
EF:ethylfluoren-9-one

Table A.36: (continued)

Sample	1,8-DMF %	A-C_2-F %	B-C_2-F %	C-C_2-F %	$D - C_2$-F %	E-C_2-F %
E 49710	18.4	16.5	98.8	49.8	100.0	32.8
E 49748	37.9	23.7	30.2	53.2	100.0	71.8
E 49749	63.6	32.1	72.0	68.8	100.0	85.2
E 49750	52.2	29.7	60.3	60.2	100.0	64.8
E 49751	46.1	27.2	58.0	63.6	100.0	51.1
E 48990	20.6	31.3	69.1	38.3	100.0	61.6
E 48478	93.4	50.7	60.8	97.1	100.0	n.d.
E 47479	46.7	18.8	32.9	39.2	91.0	38.8
E 48996	75.5	63.8	35.7	70.9	100.0	57.8
E 48388	38.6	48.5	77.7	62.3	100.0	64.7
E 48389	20.5	25.1	37.5	22.2	39.8	26.7
E 48390	20.6	37.1	47.1	28.3	56.8	34.1
E 48214	24.9	30.1	43.5	28.4	56.4	35.3
E 48216	30.2	57.5	71.9	28.6	93.2	54.5
E 48430	44.2	45.4	52.1	49.1	89.7	63.2
E 48403	43.2	53.6	82.5	60.6	100.0	46.6
E 48220	47.3	65.5	81.2	56.0	100.0	59.3
E 48392	49.6	40.4	58.9	45.2	86.6	45.2
E 48393	56.4	78.8	79.0	37.2	100.0	56.2
E 48394	77.3	44.1	64.2	25.8	100.0	45.6
E 48395	26.7	29.5	45.5	27.9	64.2	26.4
E 48396	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E 48397	21.0	22.7	44.9	32.1	60.9	26.3
E 48398	49.4	48.4	100.0	34.3	64.3	84.5
E 48400	36.4	30.1	51.1	31.3	76.0	28.5
E 48401	52.5	46.6	52.3	33.0	70.3	44.1
E 48405	10.0	11.7	18.0	13.2	21.5	9.4
E 48425	12.6	29.3	50.4	43.1	41.7	16.1
E 48382	9.8	6.6	18.4	8.9	28.2	10.9
E 48383	7.7	6.4	13.6	8.1	20.6	10.1
E 48384	8.1	6.0	13.7	10.3	19.1	9.3
E 48985	73.9	35.4	43.9	45.2	100.0	23.1
E 48986	10.6	6.8	15.8	23.7	10.1	26.8
E 48987	11.0	10.1	12.3	13.9	23.5	12.5
E 48988	36.2	25.6	28.7	51.5	100.0	70.8
E 48989	4.3	77.5	4.5	7.7	9.7	4.6
E 48993	4.8	3.3	3.9	9.5	98.8	3.7
E 48991	31.3	36.5	52.9	40.5	100.0	62.0
E 48992	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.:not detected

DMF:dimethylfluoren-9-one, F:fluoren-9-one

Table A.36: (continued)

Sample	F-C_2-F %	G-C_2-F %	H-C_2-F %	I-C_2-F %	J-C_2-F %
E 49710	37.6	9.3	22.0	4.5	77.4
E 49748	43.3	20.0	11.1	24.6	7.6
E 49749	78.5	24.0	17.3	34.5	21.5
E 49750	n.d.	20.8	15.9	34.5	n.d.
E 49751	n.d.	21.1	14.3	37.5	15.8
E 48990	56.1	15.7	13.5	18.4	76.8
E 48478	n.d.	n.d.	n.d.	n.d.	n.d.
E 47479	22.5	12.4	40.5	100.0	12.7
E 48996	28.7	50.7	45.9	38.4	100.0
E 48388	68.0	27.2	29.7	44.6	26.6
E 48389	40.1	10.9	8.9	23.4	25.3
E 48390	15.9	11.5	14.1	23.3	28.1
E 48214	29.3	12.0	8.3	25.3	25.4
E 48216	33.9	15.4	18.2	17.1	16.0
E 48430	22.5	23.8	100.0	81.2	21.2
E 48403	n.d.	30.0	25.9	59.0	28.8
E 48220	33.5	25.1	28.9	64.8	50.6
E 48392	60.5	n.d.	n.d.	n.d.	4.1
E 48393	50.0	12.5	15.8	59.8	65.7
E 48394	56.1	15.0	2.7	58.9	52.7
E 48395	5.7	10.7	12.9	24.0	19.8
E 48396	n.d.	n.d.	n.d.	n.d.	n.d.
E 48397	9.7	9.4	16.6	36.7	35.1
E 48398	34.2	15.3	20.9	32.4	22.3
E 48400	9.3	10.8	16.2	50.9	31.3
E 48401	8.7	11.8	12.5	28.4	29.4
E 48405	n.d.	4.9	3.8	9.3	5.5
E 48425	n.d.	20.1	6.5	24.6	3.2
E 48382	4.9	4.1	4.0	11.1	8.2
E 48383	1.7	3.0	2.9	11.6	9.1
E 48384	n.d.	1.7	2.5	5.7	4.5
E 48985	44.3	23.1	27.2	40.6	11.8
E 48986	12.3	3.8	11.6	2.4	n.d.
E 48987	25.3	8.5	3.9	10.4	n.d.
E 48988	n.d.	n.d.	n.d.	n.d.	n.d.
E 48989	8.9	3.4	2.2	4.8	3.0
E 48993	38.0	12.2	46.4	76.2	7.8
E 48991	11.5	20.1	20.5	27.9	13.4
E 48992	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.:not detected
F:fluoren-9-one

Table A.37: Distribution of Alkylxanthones

Sample	X	1-MX	4-MX	2-MX	3-MX
	%	%	%	%	%
E 49710	39.2	19.3	100.0	50.7	25.8
E 49748	38.4	4.4	38.6	100.0	15.4
E 49749	67.8	26.3	92.7	100.0	26.2
E 49750	62.8	23.0	73.4	100.0	23.4
E 49751	n.d.	n.d.	n.d.	n.d.	n.d.
E 48990	n.d.	n.d.	n.d.	n.d.	n.d.
E 48478	n.d.	n.d.	n.d.	n.d.	n.d.
E 47479	n.d.	n.d.	n.d.	n.d.	n.d.
E 48996	40.6	16.9	54.6	100.0	54.0
E 48388	65.6	31.9	75.7	100.0	28.4
E 48389	74.2	21.9	52.7	100.0	22.0
E 48390	81.1	22.9	59.9	100.0	35.2
E 48214	75.4	29.3	70.9	100.0	28.6
E 48216	n.d.	n.d.	n.d.	n.d.	n.d.
E 48430	n.d.	n.d.	n.d.	n.d.	n.d.
E 48403	n.d.	n.d.	n.d.	n.d.	n.d.
E 48220	58.7	29.5	88.5	100.0	51.9
E 48392	n.d.	n.d.	n.d.	n.d.	n.d.
E 48393	47.6	48.7	57.3	100.0	37.3
E 48394	61.4	26.9	69.6	100.0	41.4
E 48395	n.d.	n.d.	n.d.	n.d.	n.d.
E 48396	n.d.	n.d.	n.d.	n.d.	n.d.
E 48397	n.d.	n.d.	n.d.	n.d.	n.d.
E 48398	64.6	29.5	100.0	68.6	18.8
E 48400	77.6	41.7	100.0	87.5	36.1
E 48401	29.5	14.2	100.0	55.0	19.0
E 48405	n.d.	n.d.	n.d.	n.d.	n.d.
E 48425	n.d.	n.d.	n.d.	n.d.	n.d.
E 48382	n.d.	n.d.	n.d.	n.d.	n.d.
E 48383	n.d.	n.d.	n.d.	n.d.	n.d.
E 48384	n.d.	n.d.	n.d.	n.d.	n.d.
E 48985	n.d.	n.d.	n.d.	n.d.	n.d.
E 48986	n.d.	n.d.	n.d.	n.d.	n.d.
E 48987	n.d.	n.d.	n.d.	n.d.	n.d.
E 48988	n.d.	n.d.	n.d.	n.d.	n.d.
E 48989	n.d.	n.d.	n.d.	n.d.	n.d.
E 48993	64.0	4.2	31.1	100.0	53.8
E 48991	41.9	31.9	100.0	76.1	27.2
E 48992	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detected; X:xanthone, MX:methylxanthone

Table A.38: Distribution of Alkylnaphthaledhydes and -naphthylketones

Sample	1-NA	2-NA	A-C_1-NA	B-C_1-NA	C-C_1-NA	D-C_1-NA
	%	%	%	%	%	%
E 49710	69.5	100.0	17.9	19.8	79.7	79.0
E 49748	45.1	52.0	46.0	10.4	100.0	50.5
E 49749	44.6	76.6	36.3	11.2	100.0	843.8
E 49750	42.6	66.3	24.5	9.1	100.0	32.5
E 49751	16.8	25.9	34.2	11.5	100.0	28.6
E 48478	34.7	50.5	48.5	18.4	46.0	91.4
E 47479	30.3	37.9	36.6	14.7	73.3	43.5
E 48996	37.0	100.0	31.7	7.5	20.5	38.1
E 48388	67.2	100.0	5.6	22.0	28.0	64.4
E 48389	63.4	100.0	2.5	12.1	14.0	44.1
E 48390	70.2	100.0	4.9	14.1	25.2	43.3
E 48214	74.2	100.0	5.0	18.7	25.9	59.1
E 48216	71.3	100.0	3.4	13.6	14.4	42.2
E 48430	55.6	97.6	10.1	29.8	46.0	91.4
E 48403	16.0	100.0	1.1	9.4	19.7	46.9
E 48220	33.3	55.1	7.2	21.9	46.7	94.5
E 48393	30.0	34.1	6.2	13.1	31.5	100.0
E 48394	14.3	29.9	8.4	7.9	46.2	100.0
E 48395	29.7	51.5	6.7	11.2	100.0	74.7
E 48398	24.6	60.9	6.8	14.5	100.0	57.4
E 48400	67.2	70.1	10.5	27.0	42.8	87.5
E 48401	80.0	68.4	9.6	27.3	30.7	82.3
E 48405	27.8	100.0	0.8	4.8	11.0	14.4
E 48425	9.7	100.0	n.d.	n.d.	26.8	12.8
E 48382	62.2	100.0	4.6	5.3	28.8	25.1
E 48383	90.5	100.0	6.5	22.3	44.0	87.6
E 48384	48.2	100.0	4.5	6.9	26.0	28.7
E 48986	54.4	100.0	7.5	12.3	58.3	28.0
E 48987	36.7	100.0	5.1	7.8	56.9	27.4
E 48988	44.4	49.2	43.2	9.3	100.0	53.2
E 48989	35.8	100.0	2.3	7.3	30.7	18.5
E 48993	32.4	82.0	18.7	20.9	100.0	50.5
E 48991	50.2	100.0	n.d.	6.2	26.5	30.3
E 48992	57.2	100.0	9.4	6.3	68.8	23.9

n.d.:not detected
NA:naphthaldehyde

Table A.38: (continued)

Sample	E-C_1-NA	F-C_1-NA	G-C_1-NA	H-C_1-NA	I-C_1-NA	J-C_1-NA
	%	%	%	%	%	%
E 49710	43.0	24.6	n.d.	48.9	10.0	60.1
E 49748	25.9	23.7	n.d.	38.2	9.1	70.4
E 49749	28.1	28.9	n.d	48.5	5.2	68.2
E 49750	17.6	19.2	n.d.	36.8	6.8	45.5
E 49751	20.4	27.0	n.d.	51.0	2.5	57.4
E 48478	58.9	28.7	20.3	63.6	11.9	100.0
E 47479	27.8	28.9	n.d.	53.8	5.1	100.0
E 48996	9.9	22.9	23.8	35.9	12.9	64.6
E 48388	41.2	35.4	n.d.	86.3	5.8	68.9
E 48389	28.2	22.6	21.2	37.3	2.8	37.4
E 48390	31.6	19.5	32.7	33.1	3.1	39.1
E 48214	18.0	25.9	20.2	28.2	4.8	58.8
E 48216	29.4	23.8	26.8	34.8	4.5	47.6
E 48430	55.7	50.6	41.8	53.3	10.3	100.0
E 48403	9.6	56.1	31.1	76.2	29.8	73.0
E 48220	38.2	55.3	42.7	100.0	6.8	85.9
E 48393	35.0	32.2	26.7	52.5	9.2	63.2
E 48394	15.4	33.8	19.0	53.9	6.5	43.0
E 48395	20.6	23.0	34.9	86.5	22.5	68.3
E 48398	30.7	30.1	n.d.	73.4	5.2	60.4
E 48400	53.3	30.1	50.1	61.5	11.0	100.0
E 48401	51.9	80.6	83.4	52.1	9.9	100.0
E 48405	10.4	13.5	13.6	22.0	n.d.	19.8
E 48382	12.4	8.3	9.0	11.1	3.4	17.5
E 48383	66.6	35.8	47.1	65.6	15.0	99.7
E 48384	21.4	12.0	16.3	18.9	4.8	35.9
E 48986	28.6	29.0	15.0	34.1	13.1	60.2
E 48987	20.8	20.2	8.2	37.6	8.2	51.2
E 48988	27.0	23.0	14.6	23.5	1.7	84.2
E 48989	10.2	12.3	n.d.	25.1	2.0	32.6
E 48993	26.1	30.0	14.0	42.4	14.2	63.4
E 48991	22.2	15.9	20.4	27.1	4.7	47.8
E 48992	27.5	11.8	15.4	23.3	7.9	37.4

n.d.:not detected
NA:naphthaldehyde

Table A.38: (continued)

Sample	K-C_1-NA %	L-C_1-NA %	M-C_1-NA %
E 49710	10.9	25.2	9.8
E 49748	13.1	41.3	15.4
E 49749	13.8	15.5	10.1
E 49750	6.3	13.9	5.8
E 49751	6.3	13.9	5.8
E 48478	19.3	26.3	15.3
E 47479	18.2	15.6	13.6
E 48996	5.8	27.1	40.0
E 48388	9.8	19.1	6.6
E 48389	6.0	7.6	2.0
E 48390	7.7	10.8	3.0
E 48214	6.3	14.6	4.3
E 48216	6.8	13.6	4.0
E 48430	19.3	26.3	15.3
E 48403	10.7	10.0	4.4
E 48220	13.0	28.4	9.3
E 48393	12.4	13.1	7.4
E 48394	8.8	16.6	8.1
E 48395	10.8	20.2	9.3
E 48398	8.3	16.6	18.6
E 48400	19.1	26.8	11.7
E 48401	19.4	29.3	13.6
E 48405	3.0	1.6	n.d.
E 48382	3.6	4.3	3.8
E 48383	20.1	21.6	14.1
E 48384	6.2	5.3	3.4
E 48986	11.3	17.1	21.8
E 48987	9.0	13.5	15.3
E 48988	14.7	44.5	15.1
E 48989	3.6	4.3	15.7
E 48993	10.4	46.5	41.1
E 48991	6.5	8.9	n.d.
E 48992	8.2	10.5	10.9

n.d.:not detected
NA:naphthaldehyde

Table A.39: Distribution of Thymol, Carvacrol and 2-Isopropyl-4-Methylphenol (2-ip-4M-Phenol)

Sample	Thymol %	Carvacrol %	2ip-4M-Phenol %
E 48388	70.4	47.3	100.0
E 48389	60.6	22.5	100.0
E 48390	62.0	13.4	100.0
E 48214	53.4	11.8	100.0
E 48216	100.0	29.0	73.5
E 48220	81.7	7.8	100.0
E 48392	100.0	31.6	80.5
E 48393	3.8	0.0	100.0
E 48394	100.0	36.9	79.2
E 48395	79.2	14.1	100.0
E 48397	85.3	0.0	100.0
E 48398	100.0	39.2	80.6
E 48400	57.8	9.0	100.0
E 48401	53.2	20.4	100.0
E 48383	56.9	25.4	100.0
E 48384	100.0	27.7	48.2
E 48986	100.0	92.3	0.0
E 48988	27.6	100.0	0.0
E 48989	20.4	100.0	9.9
E 48993	43.3	10.2	100.0
E 48991	100.0	24.0	57.2
E 48992	57.5	33.1	100.0

A.5 Carboxylic Acids

Table A.40: Nomenclature of *n*-Fatty Acids

Compound	Abbreviation
Heptanoic acid	(7:0)
Octanoic acid	(8:0)
Nonanoic acid	(9:0)
Decanoic acid	(10:0)
Undecanoic acid	(11:0)
Dodecanoic acid	(12:0)
Tridecanoic acid	(13:0)
Tetradecanoic acid	(14:0)
Pentadecanoic acid	(15:0)
Hexadecanoic acid	(16:0)
Heptadecanoic acid	(17:0)
Octadecanoic acid	(18:0)
Nonadecanoic acid	(19:0)
Eicosanoic acid	(20:0)
Heneicosanoic acid	(21:0)
Docosanoic acid	(22:0)
Tricosanoic acid	(23:0)
Tetracosanoic acid	(24:0)
Pentacosanoic acid	(25:0)
Hexacosanoic acid	(26:0)
Heptacosanoic acid	(27:0)
Octacosanoic acid	(28:0)
Nonacosanoic acid	(29:0)
Triacontanoic acid	(30:0)
Hentricontanoic acid	(31:0)
Dotricontanoic acid	(32:0)

Table A.41: Distribution of *n*-Fatty Acids

Sample	(7:0) %	(8:0) %	(9:0) %	(10:0) %	(11:0) %	(12:0) %
E 49710	1.2	3	3.5	0.5	0.0	4.1
E 49748	0.1	0.7	1.0	0.5	0.3	5.4
E 49749	0.0	0.0	0.0	0.0	0.0	6.8
E 49750	0.0	0.0	0.0	1.7	1.3	15.0
E 49751	17.7	48.4	81.4	21.4	12.6	30.6
E 48478	0.0	0.3	4.0	5.8	18.6	42.3
E 48479	3.0	7.9	21.0	17.2	35.0	57.4
E 48480	3.0	6.9	24.1	9.1	4.2	19.4
E 48990	0.0	0.8	1.1	1.9	0.9	8.6
E 48996	0.0	0.0	6.3	2.0	0.5	4.8
E 48388	61.3	30.3	43.6	35.9	17.9	28.8
E 48389	100.0	14.0	24.0	27.7	14.3	24.3
E 48390	100.0	10.7	17.0	8.0	8.1	17.3
E 48214	64.3	14.3	27.4	19.3	15.6	23.7
E 48216	100.0	18.7	36.2	56.1	21.8	32.9
E 48403	4.4	9.2	18.2	6.5	2.5	9.9
E 48220	100.0	12.2	19.6	33.6	12.7	21.2
E 48430	0.0	0.0	20.5	14.7	5.2	23.3
E 48392	100.0	10.2	18.0	24.1	8.5	17.2
E 48393	87.2	8.4	20.2	12.3	6.3	18.0
E 48394	100.0	18.2	44.3	11.9	3.8	9.8
E 48395	57.1	5.4	12.0	7.3	5.0	13.1
E 48396	100.0	10.1	22.9	10.0	8.8	15.6
E 48397	11.7	10.7	14.6	6.1	3.6	10.9
E 48398	24.1	4.0	9.1	4.3	2.4	10.6
E 48400	9.5	21.2	3	6.7	1.5	9.6
E 48401	6.1	12.9	23.0	4.2	1.1	7.3
E 48405	50.4	6.5	13.1	3.8	1.6	10.4
E 48425	0.0	0.0	0.0	0.0	0.0	3.6
E 48382	2.6	1.9	5.6	2.9	1.7	6.1
E 48383	60.5	33.7	55.6	33.1	24.2	35.4
E 48384	5.7	5.7	14.2	4.9	3.6	9.6
E 48985	0.0	0.0	0.4	1.6	4.6	10.0
E 48986	0.0	0.0	27.2	19.8	30.5	46.7
E 48987	0.0	0.0	8.3	5.6	9.4	17.5
E 48988	0.0	0.0	54.8	11.8	16.3	28.9
E 48989	0.0	0.0	26.3	3.1	1.7	3.7
E 48993	0.0	0.0	0.0	0.0	0.0	0.0
E 48991	0.0	0.3	1.0	1.2	0.7	8.1
E 48992	11.5	9.8	12.7	6.9	4.4	14.2

Table A.41: (continued)

Sample	(13:0) %	(14:0) %	(15:0) %	(16:0) %	(17:0) %	(18:0) %
E 49710	0.0	33.3	8.4	100.0	1.3	62.5
E 49748	0.9	66.7	22.0	100.0	8.8	24.6
E 49749	0.0	0.0	0.0	100.0	0.0	25.6
E 49750	2.7	32.1	10.2	100.0	6.6	19.6
E 49751	11.9	49.0	32.9	100.0	21.2	36.1
E 48478	37.5	69.9	70.3	100.0	87.0	98.9
E 48479	47.7	83.2	87.9	100.0	27.1	78.1
E 48480	5.7	38.7	18.2	100.0	5.2	34.6
E 48990	1.3	21.5	9.9	100.0	5.4	66.1
E 48996	0.5	9.0	4.5	54.1	5.1	37.7
E 48388	15.7	44.6	25.3	100.0	15.6	58.5
E 48389	10.8	30.8	20.6	94.2	12.4	46.9
E 48390	7.8	25.0	14.8	89.6	10.5	49.1
E 48214	12.4	31.8	23.0	100.0	18.1	54.0
E 48216	23.0	61.4	46.2	96.6	21.7	55.6
E 48403	1.8	21.1	7.6	100.0	3.1	32.4
E 48220	10.8	26.1	19.6	88.5	17.4	62.4
E 48430	3.7	25.4	9.1	100.0	3.4	19.8
E 48392	6.4	29.9	14.4	96.7	12.7	47.6
E 48393	4.7	29.9	13.8	100.0	7.0	72.3
E 48394	1.1	10.8	3.9	42.6	6.2	19.8
E 48395	3.2	21.3	13.5	100.0	6.3	42.7
E 48396	6.4	28.1	16.2	97.9	10.9	78.5
E 48397	3.0	20.8	10.3	100.0	9.0	69.6
E 48398	2.1	18.9	10.4	100.0	7.9	50.9
E 48400	1.2	24.0	5.6	100.0	2.6	43.1
E 48401	0.6	15.7	5.0	100.0	1.8	36.5
E 48405	1.3	20.2	7.4	100.0	2.4	37.9
E 48425	0.5	16.0	6.5	100.0	4.0	83.2
E 48382	1.7	17.7	10.8	100.0	5.3	35.7
E 48383	21.2	53.5	35.9	100.0	23.4	56.5
E 48384	2.7	25.3	9.3	100.0	4.5	38.1
E 48985	7.8	19.5	20.5	60.4	38.2	69.8
E 48986	33.1	56.6	56.3	100.0	70.2	93.4
E 48987	11.4	28.1	30.0	88.0	52.8	86.8
E 48988	11.3	38.2	23.9	100.0	15.1	49.6
E 48989	1.4	4.9	3.3	20.2	2.3	7.8
E 48993	0.0	0.1	0.1	0.4	0.2	0.5
E 48991	1.2	16.5	7.7	100.0	5.9	81.4
E 48992	3.8	26.3	12.7	100.0	6.8	61.3

Table A.41: (continued)

Sample	(19:0) %	(20:0) %	(21:0) %	(22:0) %	(23:0) %	(24:0) %
E 49710	0.0	0.2	0.0	0.0	0.0	0.0
E 49748	9.7	12.2	11.6	13.3	12.6	14.6
E 49749	0.0	0.0	0.0	0.0	0.0	0.0
E 49750	2.4	2.5	1.3	1.6	0.8	1.6
E 49751	13.0	13.8	10.9	10.6	9.1	12.2
E 48478	84.5	74.7	59.7	49.5	35.4	28.3
E 48479	71.7	61.6	53.8	68.4	60.0	54.0
E 48480	1.7	1.9	1.4	1.9	1.2	2.0
E 48990	0.9	2.1	0.4	1.9	0.6	0.0
E 48996	8.2	16.6	11.7	27.5	21.1	49.7
E 48388	10.7	11.1	9.1	9.8	7.1	9.2
E 48389	8.5	9.1	7.0	8.4	6.4	8.6
E 48390	8.4	9.1	6.2	6.8	4.9	6.3
E 48214	12.7	13.5	10.2	10.4	9.2	10.8
E 48216	15.1	16.5	14.2	14.4	11.1	11.6
E 48403	1.1	1.5	0.7	1	0.0	1.0
E 48220	13.0	12.6	10.2	11.5	8.8	11.0
E 48430	4.4	2.0	1.1	1.4	0.0	1.2
E 48392	4.3	4.9	3.3	4.2	3.0	4.6
E 48393	2.6	4.5	2.1	3.6	2.3	3.3
E 48394	3.2	0.0	0.0	0.0	0.0	0.0
E 48395	1.1	1.7	0.3	1.2	0.3	2.3
E 48396	4.5	6.1	4.4	5.5	3.9	4.6
E 48397	7.6	9.8	7.6	10.6	8.1	11.2
E 48398	1.6	2.3	1.0	1.8	1.1	2.5
E 48400	1.7	3.0	1.2	3.8	1.5	4.2
E 48401	0.4	0.8	0.2	0.6	0.6	1.5
E 48405	0.3	1.0	0.1	0.6	0.2	0.9
E 48425	0.7	3.4	0.6	6.9	0.9	0.0
E 48382	1.8	4.6	1.3	3.5	1.7	5.1
E 48383	18.8	20.7	19.5	20.7	16.0	17.1
E 48384	1.8	2.4	1.2	1.8	1.2	2.0
E 48985	48.8	66.5	63.8	87.5	70.9	100.0
E 48986	52.5	55.3	38.0	41.9	25.3	31.6
E 48987	61.2	81.6	74.3	97.7	72.9	100.0
E 48988	11.0	14.3	14.9	19.7	17.3	24.6
E 48989	1.7	2.3	2.6	5.6	4.0	16.7
E 48993	0.6	1.8	3.2	9.9	11.0	31.4
E 48991	1.1	2.3	0.5	2.6	0.7	0.0
E 48992	2.4	3.3	1.9	3.0	2.0	3.9

Table A.41: (continued)

Sample	(25:0) %	(26:0) %	(27:0) %	(28:0) %	(29:0) %	(30:0) %
E 49710	0.0	0.0	0.0	0.0	0.0	0.0
E 49748	10.3	11.2	8.2	9.8	7.3	7.6
E 49749	0.0	0.0	0.0	0.0	0.0	0.0
E 49750	0.5	1.0	0.2	1.1	0.0	0.0
E 49751	6.7	10.1	4.7	10.6	4.0	10.5
E 48478	20.4	14.7	11.2	8.2	5.8	4.1
E 48479	43.1	34.5	23.2	14.1	7.5	4.9
E 48480	0.8	0.9	0.4	0.5	0.3	0.3
E 48990	0.6	1.5	0.2	0.0	0.0	0.0
E 48996	32.5	70.6	31.6	100.0	29.0	64.5
E 48388	6.6	9.5	5.0	6.8	3.8	3.5
E 48389	5.6	6.8	4.0	4.3	2.7	1.8
E 48390	4.3	4.8	2.9	2.6	1.6	1.0
E 48214	9.2	9.8	6.9	6.6	5.0	3.5
E 48216	9.8	10.4	7.7	7.3	5.4	3.9
E 48403	0.2	0.3	0.0	0.0	0.0	0.0
E 48220	7.9	10.6	6.1	6.5	3.9	2.3
E 48430	0.0	1.0	0.0	0.0	0.0	0.0
E 48392	2.6	3.0	1.3	1.4	0.7	0.6
E 48393	1.7	2.1	1.1	1.3	0.7	0.6
E 48394	0.0	0.0	0.0	0.0	0.0	0.0
E 48395	0.4	0.9	0.1	0.3	0.1	0.1
E 48396	2.5	2.9	1.5	1.4	0.8	0.6
E 48397	5.9	7.3	3.6	3.4	1.6	1.0
E 48398	0.8	1.2	0.4	0.4	0.2	0.2
E 48400	1.2	6.6	1.1	3.2	0.8	0.9
E 48401	0.4	0.9	0.0	0.4	0.0	0.0
E 48405	0.1	0.3	0.0	0.1	0.0	0.0
E 48425	1.0	2.1	0.4	0.0	0.0	0.0
E 48382	2.2	4.7	1.4	2.4	0.9	0.9
E 48383	13.6	14.7	9.6	8.9	5.3	3.8
E 48384	1.0	1.2	0.5	0.5	0.3	0.3
E 48985	62.1	78.4	39.3	68.5	22.9	21.8
E 48986	14.7	17.0	7.8	13.6	5.0	7.1
E 48987	56.1	69.0	32.3	57.1	17.6	19.0
E 48988	16.5	26.9	17.7	56.7	13.3	31.6
E 48989	6.1	34.2	9.7	100.0	12.6	82.3
E 48993	17.7	93.4	18.5	100.0	1.0	1.5
E 48991	0.6	1.7	0.3	0.0	0.0	0.0
E 48992	1.9	2.9	1.4	3.2	0.9	1.2

Table A.41: (continued)

Sample	(31:0) %	(32:0) %
E 49710	0.0	0.0
E 49748	0.0	5.5
E 49749	0.0	0.0
E 49750	0.0	1.0
E 49751	2.4	7.2
E 48478	2.4	1.5
E 48479	2.0	2.2
E 48480	0.0	0.0
E 48990	0.0	0.0
E 48996	16.0	16.3
E 48388	1.8	1.7
E 48389	1.3	0.7
E 48390	0.6	0.3
E 48214	2.3	1.2
E 48216	2.7	1.3
E 48403	0.0	0.0
E 48220	1.4	0.7
E 48430	0.0	0.0
E 48392	0.3	0.3
E 48393	0.3	0.2
E 48394	0.0	0.0
E 48395	0.0	0.0
E 48396	0.3	0.2
E 48397	0.6	0.4
E 48398	0.1	0.1
E 48400	0.2	0.5
E 48401	0.0	0.0
E 48405	0.0	0.0
E 48425	0.0	0.0
E 48382	0.5	0.4
E 48383	2.2	1.3
E 48384	0.1	0.1
E 48985	7.6	8.6
E 48986	2.0	2.8
E 48987	6.0	6.9
E 48988	8.3	17.7
E 48989	5.2	20.2
E 48993	0.0	0.0
E 48991	0.0	0.0
E 48992	0.4	0.5

Table A.42: Distribution of Alkylbenzoic Acids

Sample	BA	PAA	2-MBA	3-MBA	4-MBA
	%	%	%	%	%
E 49751	100.0	1.3	19.6	28.9	10.1
E 48478	100.0	6.8	10.7	27.4	19.9
E 48479	82.4	12.2	10.1	41.4	22.2
E 48480	100.0	2.2	5.3	14.7	13.1
E 48990	100.0	20.4	7.6	73.6	55.8
E 48388	100.0	3.3	7.3	48.3	24.1
E 48389	100.0	2.8	5.4	41.8	18.0
E 48390	100.0	11.0	9.2	47.5	21.5
E 48214	100.0	1.7	8	75.0	27.7
E 48216	100.0	9.0	10.0	64.3	28.4
E 48403	100.0	0.5	7.4	85.6	39.4
E 48220	90.0	4.3	4.5	45.5	35.4
E 48430	100.0	1.2	8.6	56.5	24.6
E 48392	100.0	3.0	9.9	23.9	12.3
E 48393	100.0	2.0	9.5	16.1	7.6
E 48395	100.0	3.5	2.3	23.7	23.6
E 48396	100.0	2.8	10.7	19.0	13.4
E 48398	100.0	1.2	1.4	12.1	6.5
E 48405	100.0	0.7	4.7	27.8	8.9
E 48382	100.0	1.1	2.5	8.1	7.4
E 48383	100.0	2.9	6.1	56.5	25.9
E 48986	23.0	23.2	35.9	100.0	73.2
E 48988	0.0	13.0	20.1	66.1	100.0
E 48989	0.8	16.4	16.6	71.1	100.0
E 48991	100.0	3.0	10.8	39.0	24.5
E 48992	0.0	3.7	66.3	100.0	35.9

BA:benzoic acid, PAA:phenylacetic acid
MBA:methylbenzoic acid

Table A.42: (continued)

Sample	PAA	PPA	PAA	2,6-DMBA
	%	%	%	%
E 49751	1.5	0.3	1.2	0.3
E 48990	0.0	0.0	0.0	0.0
E 48478	0.0	0.0	3.0	3.5
E 48479	7.5	1.3	1.3	1.2
E 48480	0.0	1.0	2.6	0.8
E 48388	1.2	9.8	1.7	1.1
E 48389	0.6	1.9	1.9	0.7
E 48390	0.4	1.9	2.1	0.9
E 48214	0.6	2.8	2.4	0.6
E 48216	2.1	4.0	4.0	1.4
E 48403	0.7	0.3	0.0	0.2
E 48220	0.3	4.9	2.0	3.9
E 48430	0.8	0.0	0.3	2.4
E 48392	0.5	5.7	2.0	1.2
E 48393	0.5	7.0	1.3	1.2
E 48395	0.2	6.5	1.3	1.5
E 48396	0.2	3.7	1.1	0.5
E 48398	0.2	5.0	0.4	0.7
E 48405	0.2	0.4	0.7	0.1
E 48382	0.0	0.9	1.6	0.0
E 48383	1.7	2.1	1.6	1.3
E 48986	19.1	26.2	32.8	0.0
E 48988	6.9	13.5	13.5	0.1
E 48989	13.2	41.0	7.8	1.1
E 48991	5.2	0.0	2.6	0.0
E 48992	12.3	2.8	5.8	0.0

PPA:phenylpropanbenzoic acid
DMBA:dimethylbenzoic acid

Table A.42: (continued)

Sample	2,5-DMBA	4-EBA	3,4-DMBA	3,5-DMBA
	%	%	%	%
E 49751	9.4	2.5	15.9	16.1
E 48990	0.0	31.9	76.6	71.2
E 48478	13.7	5.1	36.5	24.7
E 48479	15.7	4.5	100.0	35.0
E 48480	1.8	2.0	6.8	4.6
E 48388	3.0	3.2	25.6	23.1
E 48389	2.7	2.0	21.4	8.9
E 48390	3.5	2.8	14.9	11.0
E 48214	6.1	4.9	55.9	25.9
E 48216	5.5	3.7	77.2	37.8
E 48403	3.3	10.3	44.8	30.2
E 48220	3.0	3.7	53.2	100.0
E 48430	4.8	3.2	19.5	16.6
E 48392	2.1	3.1	17.2	31.5
E 48393	1.5	1.6	6.8	16.4
E 48395	0.8	1.6	15.0	32.2
E 48396	1.3	2.3	7.5	12.6
E 48398	1.0	0.9	5.2	3.9
E 48405	1.4	0.9	7.2	3.8
E 48382	2.9	0.9	9.3	9.5
E 48383	2.3	3.5	20.8	14.1
E 48986	10.5	5.5	27.9	19.8
E 48988	4.7	3.8	0.0	10.5
E 48989	6.0	2.7	0.0	14.6
E 48991	17.9	2.5	21.8	50.9
E 48992	12.4	4.4	6.2	25.6

EBA:ethylbenzoic acid
DMBA:dimethylbenzoic acid

Table A.43: Distribution of Alkylhydroxy-/Alkylmethoxybenzoic Acids

Sample	2-HBA	4-HBA	3-HBA	A-C_1	B-C_1
	%	%	%	%	%
E 48388	100.0	26.3	26.0	68.9	56.2
E 48389	100.0	51.1	35.2	71.6	66.5
E 48390	12.8	0.0	47.1	100.0	26.6
E 48214	17.8	6.6	0.0	95.7	0.0
E 48216	17.3	23.4	12.0	27.9	56.8
E 48403	2.3	5.2	2.3	48.5	6.3
E 48220	27.8	23.8	13.7	70.1	24.3
E 48392	59.2	26.1	13.2	70.6	100.0
E 48393	20.7	30.9	33.5	73.0	0.0
E 48395	13.8	32.9	12.7	17.8	21.8
E 48396	21.1	8.8	13.3	89.2	59.3
E 48397	26.1	0.0	10.4	3.4	21.0
E 48398	31.3	38.2	16.2	11.5	14.8
E 48400	100.0	0.0	31.5	34.8	35.8
E 48401	100.0	0.0	0.0	0.0	24.8
E 48382	100.0	0.0	0.0	0.0	0.0
E 48383	51.4	39.6	94.2	48.1	46.4
E 48985	0.0	13.1	56.8	0.0	0.0
E 48986	13.2	0.0	6.2	1.8	3.5
E 48987	0.0	10.4	100.0	0.2	0.0
E 48988	17.4	38.1	100.0	2.0	3.1
E 48989	14.6	44.5	100.0	0.8	3.4

HBA:hydroxybenzoic acid

Table A.43: (continued)

Sample	C-C_1	D-C_1	E-C_1	A-C_2	B-C_2
	%	%	%	%	%
E 48388	64.0	0.7	4.6	37.8	16.9
E 48389	68.0	15.6	47.3	39.5	11.0
E 48390	0.0	4.4	83.7	11.9	0.0
E 48214	100.0	0.0	5.6	53.4	11.0
E 48216	61.7	5.3	16.3	100.0	12.7
E 48403	100.0	3.0	14.7	0.0	0.0
E 48220	100.0	4.4	13.9	74.1	9.9
E 48392	74.0	10.4	31.0	73.9	32.6
E 48393	0.0	22.5	100.0	0.0	0.0
E 48395	100.0	27.4	55.6	27.4	10.1
E 48396	72.3	13.5	38.3	100.0	20.0
E 48397	16.9	6.4	36.1	12.1	0.0
E 48398	48.5	3.1	13.1	36.4	5.1
E 48400	66.8	18.0	59.0	0.0	0.0
E 48401	81.5	0.0	46.1	0.0	0.0
E 48382	0.0	0.0	0.0	0.0	0.0
E 48383	100.0	3.6	25.8	20.3	6.8
E 48985	3.3	100.0	0.0	0.0	0.0
E 48986	17.4	100.0	0.0	4.2	0.0
E 48987	0.7	34.7	0.0	0.0	0.0
E 48988	1.3	19.8	0.0	3.7	0.0
E 48989	2.4	25.1	0.0	2.1	0.0

Table A.43: (continued)

Sample	C-C_2	D-C_2	E-C_2	F-C_2
	%	%	%	%
E 48388	1.1	21.1	0.6	9.4
E 48389	3.0	49.1	6.4	11.8
E 48390	0.0	0.0	0.0	0.0
E 48214	0.0	13.4	0.0	10.0
E 48216	1.5	32.7	19.0	20.7
E 48403	1.0	2.8	0.0	0.0
E 48220	2.3	33.4	2.9	24.3
E 48392	2.7	33.8	7.2	20.5
E 48393	5.7	50.2	22.9	0.0
E 48395	2.6	51.5	7.7	9.1
E 48396	2.3	24.4	5.0	32.1
E 48397	0.0	100.0	0.0	0.0
E 48398	1.7	100.0	5.2	32.1
E 48400	0.0	0.0	0.0	0.0
E 48401	0.0	0.0	0.0	0.0
E 48382	0.0	0.0	0.0	0.0
E 48383	3.4	36.2	3.0	14.4
E 48985	0.0	0.0	0.0	0.0
E 48986	0.0	0.0	0.0	0.0
E 48987	0.0	0.0	0.0	0.0
E 48988	0.0	0.0	0.0	0.0
E 48989	0.0	0.0	0.0	0.0

Table A.43: (continued)

Sample	4H3MBA %	3,4-DHBA %
E 48388	28.7	8.5
E 48389	3.8	8.1
E 48390	22.2	78.7
E 48214	1.2	2.6
E 48216	0.0	0.6
E 48403	0.6	3.0
E 48220	3.7	8.2
E 48392	0.4	2.9
E 48393	2.2	16.0
E 48395	0.3	3.3
E 48396	0.0	3.7
E 48397	0.0	0.0
E 48398	1.4	1.7
E 48400	0.0	0.0
E 48401	0.0	0.0
E 48382	0.0	0.0
E 48383	4.4	2.2
E 48985	0.0	1.9
E 48986	0.0	3.4
E 48987	1.1	1.8
E 48988	10.8	6.3
E 48989	6.5	4.9

4H3MBA:4-hydroxy-3-methoxybenzoic acid
3,4-DHBA:3,4-dihydroxybenzoic acid

Table A.44: Distribution of Alkylnaphthalenecarboxylic Acids

Sample	1-NCA	2-NCA	A-C_1-NCA	B-C_1-NCA	C-C_1-NCA
	%	%	%	%	%
E 49751	43.6	42.6	12.1	37.6	48.6
E 48388	48.4	100.0	11.5	16.9	13.5
E 48389	40.5	100.0	7.7	13.7	11.2
E 48390	50.0	100.0	3.3	18.0	13.2
E 48214	31.7	88.6	0	17.6	13.9
E 48216	60.8	88.9	9.9	18.8	13.3
E 48403	5.6	58.0	0.7	2.1	2.9
E 48220	16.9	100.0	4.4	12.5	12.5
E 48430	57.3	97.1	21.1	23.7	29.8
E 48392	7.1	31.1	2.1	4.2	5.8
E 48393	6.9	20.1	1.2	3.5	4.7
E 48395	9.9	100.0	1.9	3.5	4.0
E 48396	8.0	48.1	3.0	4.5	10.6
E 48398	10.3	62.0	2.7	5.1	7.0
E 48405	37.3	100.0	1.0	7.1	5.3
E 48383	54.3	100.0	17.1	20.1	19.6
E 48988	55.3	100.0	0.0	18.8	8.1
E 48992	99.7	100.0	14.3	11.0	7.9

NCA:naphthalenecarboxylic acid

Table A.44: (continued)

Sample	D-C_1-NCA %	E-C_1-NCA %	F-C_1-NCA %	G-C_1-NCA %	H-C_1-NCA %
E 49751	36.7	50.9	9.0	26.7	12.6
E 48388	14.5	22.1	7.3	25.1	6.4
E 48389	11.2	15.6	3.9	22.3	4.2
E 48390	22.3	22.1	2.8	23.1	5.2
E 48214	0.0	28.0	4.1	27.6	4.4
E 48216	25.6	24.8	6.8	28.0	5.7
E 48403	3.0	2.5	0.8	18.4	0.9
E 48220	18.3	15.2	4.0	26.5	3.3
E 48430	30.0	39.2	10.0	28.1	15.0
E 48392	6.5	4.7	1.8	17.7	1.4
E 48393	5.4	3.7	1.1	11.4	1.5
E 48395	4.7	2.7	1.1	18.7	2.0
E 48396	8.5	5.0	2.8	35.3	2.5
E 48398	5.8	2.8	1.7	19.6	1.6
E 48405	7.5	9.8	0.7	10.5	1.3
E 48383	20.0	30.9	11.2	29.5	8.2
E 48988	10.0	17.4	5.3	10.0	8.6
E 48992	15.5	28.0	7.7	9.6	0.9

NCA:naphthalenecarboxylic acid

Table A.44: (continued)

Sample	I-C_1-NCA %	J-C_1-NCA %	K-C_1-NCA %
E 49751	100.0	31.7	23.9
E 48388	80.5	15.9	23.5
E 48389	78.1	14.4	21.9
E 48390	87.5	14.5	20.5
E 48214	100.0	16.0	26.5
E 48216	100.0	16.4	25.9
E 48403	100.0	13.1	26.4
E 48220	94.5	21.1	22.0
E 48430	100.0	18.0	30.1
E 48392	100.0	21.1	15.2
E 48393	100.0	14.8	13.2
E 48395	69.3	19.7	19.2
E 48396	100.0	90.9	23.3
E 48398	100.0	23.7	15.4
E 48405	52.49	9.0	9.6
E 48383	86.5	17.3	29.7
E 48988	52.5	13.1	14.5
E 48992	34.3	8.3	15.7

NCA:naphthalenecarboxylic acid

Table A.45: Distribution of Alkylanthracene/Phenanthrenecarboxylic Acids

Sample	A-C_0	9-PCA	B-C_0	C-C_0	D-C_0
	%	%	%	%	%
E 49751	79.6	41.2	100.0	66.3	0.0
E 48388	57.0	42.3	96.7	100.0	38.8
E 48389	45.9	35.1	100.0	93.8	47.2
E 48390	50.1	39.5	100.0	98.7	46.4
E 48214	47.8	39.2	98.1	100.0	44.1
E 48216	64.6	47.7	100.0	97.9	54.8
E 48403	28.0	17.1	100.0	81.4	3.7
E 48220	29.9	25.7	48.4	100.0	24.7
E 48430	86.7	63.7	68.2	100.0	62.3
E 48392	60.8	47.9	87.6	100.0	43.5
E 48393	62.7	53.8	77.2	100.0	34.0
E 48395	31.9	22.2	85.0	100.0	15.6
E 48396	29.2	22.0	42.6	100.0	55.2
E 48398	36.4	8.4	45.5	100.0	18.9
E 48405	47.55	27.26	100.0	82.45	2.1
E 48425	15.5	7.2	91.6	100.0	2.8
E 48383	64.2	53.7	91.4	100.0	31.4
E 48992	100.0	77.6	90.4	71.6	8.6

PCA:phenanthrenecarboxylic acid

Table A.45: (continued)

Sample	A-C_1 %	B-C_1 %	C-C_1 %	D-C_1 %	E-C_1 %
E 49751	19.3	50.6	86.9	21.0	61.9
E 48388	9.2	12.4	41.0	16.0	44.3
E 48389	8.8	9.1	32.2	13.0	36.3
E 48390	12.7	12.9	35.0	15.9	41.6
E 48214	12.4	10.2	41.0	21.6	44.0
E 48216	17.3	12.9	48.9	46.3	53.0
E 48403	4.8	3.8	13.2	5.2	22.4
E 48220	6.5	5.0	19.6	35.8	23.2
E 48430	0.0	0.0	7.5	79.3	38.9
E 48392	9.9	5.0	28.4	61.1	29.7
E 48393	12.1	8.1	32.9	76.6	29.2
E 48395	7.4	2.8	14.1	10.4	20.4
E 48396	5.1	3.3	13.4	27.2	13.4
E 48398	2.6	1.0	7.3	21.1	8.5
E 48405	4.6	4.4	13.1	4.9	17.7
E 48425	1.9	1.9	4.1	2.0	17.0
E 48383	10.2	9.0	30.0	30.5	35.8
E 48992	0.0	0.0	23.5	0.0	24.0

Table A.45: (continued)

Sample	F-C_1 %	G-C_1 %	H-C_1 %	I-C_1 %	J-C_1 %
E 49751	13.9	15.5	13.3	35.4	30.9
E 48388	20.3	28.3	15.2	50.9	18.1
E 48389	16.5	24.2	17.1	40.1	9.4
E 48390	22.3	22.4	16.4	33.8	8.6
E 48214	18.3	23.4	16.4	38.1	11.4
E 48216	32.4	28.5	18.3	47.7	15.7
E 48403	5.7	12.6	7.5	20.1	5.9
E 48220	12.1	11.1	8.2	19.1	4.9
E 48430	24.4	26.8	17.6	35.6	40.7
E 48392	16.2	12.9	15.3	27.8	9.1
E 48393	18.0	16.3	12.4	25.6	10.8
E 48395	5.4	8.5	10.7	21.8	6.5
E 48396	8.2	6.5	9.4	13.2	4.4
E 48398	4.5	3.6	7.7	13.2	5.9
E 48405	3.8	8.0	3.6	12.8	3.7
E 48425	1.8	13.6	0.0	8.6	2.3
E 48383	19.5	20.0	16.6	33.3	10.5
E 48992	0.0	0.0	0.0	0.0	0.0

Table A.45: (continued)

Sample	K-C_1 %	L-C_1 %
E 49751	51.2	34.9
E 48388	58.5	42.8
E 48389	52.2	28.8
E 48390	51.0	24.6
E 48214	53.5	32.6
E 48216	65.1	38.9
E 48403	38.8	31.6
E 48220	24.9	16.1
E 48430	47.1	40.8
E 48392	37.9	22.1
E 48393	35.9	24.9
E 48395	29.7	16.2
E 48396	19.0	23.0
E 48398	13.3	11.2
E 48405	17.2	8.9
E 48425	16.9	4.0
E 48383	47.9	33.2
E 48992	19.6	22.0

Table A.46: Distribution of Alkylnaphthalenedicarboxylic Acids

Sample	A-C_0	B-C_0	C-C_0	A-C_1	B-C_1
	%	%	%	%	%
E 48388	100.0	0.0	13.7	8.9	23.8
E 48389	100.0	11.8	11.9	29.3	24.5
E 48390	10.9	0.0	0.0	100.0	30.8
E 48214	22.9	79.7	4.5	100.0	15.3
E 48216	56.3	100.0	25.6	86.5	23.9
E 48403	100.0	0.0	30.7	20.0	19.1
E 48220	31.6	95.7	19.6	100.0	11.9
E 48430	100.0	0.0	34.7	0.0	26.9
E 48392	84.0	100.0	45.4	42.2	19.7
E 48393	29.3	100.0	13.5	84.9	13.6
E 48395	100.0	0.0	20.1	48.7	20.4
E 48396	41.5	0.0	21.4	100.0	16.1
E 48398	100.0	10.1	27.3	25.4	30.7
E 48400	2.1	19.1	0.0	100.0	10.8
E 48405	100.0	0.0	11.1	59.3	23.7
E 48425	94.0	100.0	28.2	83.8	47.2
E 48382	4.0	13.7	1.3	100.0	0.0
E 48383	100.0	0.0	19.0	49.0	27.2
E 48384	2.1	24.9	1.0	100.0	0.0
E 48985	0.0	100.0	0.0	63.8	0.0
E 48986	0.0	100.0	0.0	9.2	0.0
E 48987	0.0	100.0	0.0	78.4	0.0
E 48988	32.9	100.0	21.4	47.7	0.0
E 48989	40.7	100.0	37.4	43.6	0.0
E 48992	12.3	100.0	6.5	37.0	0.0

Table A.46: (continued)

Sample	C-C_1	D-C_1	E-C_1	F-C_1	G-C_1
	%	%	%	%	%
E 48388	21.7	19.4	20.7	5.1	1.3
E 48389	25.6	21.0	31.4	6.0	0.6
E 48390	5.0	13.6	53.1	0.0	0.0
E 48214	6.8	5.7	28.0	0.0	0.0
E 48216	20.3	15.7	65.9	12.7	4.9
E 48403	23.7	20.7	23.0	21.3	6.8
E 48220	13.3	24.2	39.0	10.6	9.3
E 48430	28.1	25.0	31.5	15.3	18.7
E 48392	16.7	13.1	13.5	11.0	2.5
E 48393	65.3	9.9	31.9	4.8	0.0
E 48395	13.3	12.9	7.3	6.0	3.6
E 48396	15.8	7.8	41.2	0.0	3.8
E 48398	20.2	19.9	44.6	12.8	0.0
E 48400	0.8	0.0	27.5	0.0	0.0
E 48405	20.2	31.5	32.2	16.1	0.0
E 48425	38.3	0.0	43.0	8.4	0.0
E 48382	0.0	0.0	0.0	0.0	0.0
E 48383	26.8	20.0	31.6	11.6	2.5
E 48384	0.0	35.7	36.3	0.0	1.4
E 48985	0.0	0.0	0.0	0.0	0.0
E 48986	0.0	0.0	0.0	0.0	0.0
E 48987	0.0	0.0	0.0	0.0	0.0
E 48988	0.0	0.0	0.0	0.0	0.0
E 48989	0.0	0.0	0.0	0.0	0.0
E 48992	0.0	0.0	0.0	0.0	0.0

Table A.46: (continued)

Sample	A-C_2 %	B-C_2 %	C-C_2 %	D-C_2 %
E 48388	3.1	3.3	2.5	13.6
E 48389	3.4	10.6	10.5	26.5
E 48390	2.9	36.4	37.3	86.1
E 48214	0.0	32.0	33.1	57.3
E 48216	5.6	34.5	36.9	77.9
E 48403	0.0	3.7	4.2	7.2
E 48220	6.4	20.0	24.3	46.5
E 48430	0.0	0	0.0	0.0
E 48392	3.4	11.5	12.9	26.0
E 48393	3.2	14.3	16.1	29.3
E 48395	0.0	7.9	9.6	17.3
E 48396	7.7	17.5	21.9	37.0
E 48398	0.0	0	0.0	0.0
E 48400	0.0	14.1	18.5	33.8
E 48405	0.0	12.3	17.6	15.4
E 48425	0.0	0	0.0	0.0
E 48382	0.0	10.2	10.2	14.3
E 48383	3.6	9.5	9.1	22.3
E 48384	0.0	12.8	14.4	23.4
E 48985	0.0	0	0.0	0.0
E 48986	0.0	0	0.0	0.0
E 48987	0.0	0	0.0	0.0
E 48988	0.0	0	0.0	0.0
E 48989	0.0	0	0.0	0.0
E 48992	0.0	0	0.0	0.0

Table A.47: Distribution of Hopanoic Acids

Sample	$\alpha\beta$-C_{31}	$\alpha\beta$-C_{31}	$\beta\alpha$-C_{31}	$\beta\alpha$-C_{31}	$\alpha\beta$-C_{32}	$\alpha\beta$-C_{32}
	%	%	%	%	%	%
E 48478	100.0	51.1	16.1	18.1	34.7	23.1
E 48479	100.0	79.0	29.1	33.0	55.6	30.0
E 48388	100.0	87.3	36.0	44.7	11.5	8.4
E 48389	100.0	87.7	36.6	47.0	18.6	14.2
E 48390	100.0	85.5	31.2	39.1	18.1	13.3
E 48214	100.0	90.2	37.2	47.4	21.4	17.2
E 48216	100.0	91.8	36.8	45.5	13.2	10.8
E 48220	100.0	84.7	31.3	36.2	17.3	13.2
E 48392	100.0	86.1	32.8	37.1	44.1	30.9
E 48393	100.0	86.6	28.2	34.3	21.8	15.2
E 48395	66.8	100.0	0.0	0.0	0.0	0.0
E 48396	100.0	82.1	29.1	37.3	23.9	9.7
E 48397	100.0	48.7	23.2	10.1	0.0	0.0
E 48398	100.0	83.8	0.0	0.0	0.0	0.0
E 48400	100.0	0.0	0.0	0.0	0.0	0.0
E 48382	100.0	80.6	33.4	35.0	12.2	10.8
E 48383	100.0	84.7	34.4	41.1	14.0	10.1
E 48985	0	37.8	19.1	66.5	100.0	0.0
E 48986	5.0	40.0	20.5	72.3	100.0	0.0
E 48987	0.0	37.6	18.5	74.1	100.0	0.0
E 48988	0.0	18.4	13.8	100.0	66.2	0.0
E 48989	0.0	0.0	0.0	98.8	100.0	0.0
E 48992	100.0	87.6	30.0	4	7.5	13.8

Table A.48: Distribution of additional Hopanoic Acids present in Immature Coals

Sample	$\alpha\beta$-C_{30} %	$\alpha\beta$-C_{30} %	$\beta\alpha$-C_{30} %	$\beta\alpha$-C_{30} %
E 48985	0.0	0.0	42.3	29.2
E 48986	7.5	6.1	51.9	31.5
E 48987	8.2	7.0	52.7	33.8
E 48988	0.0	0.0	14.2	22.1
E 48989	0.0	0.0	0.0	0.0

Table A.48: (continued)

Sample	$\beta\alpha$-C_{32} %	$\beta\beta\beta$-C_{32} %	$\alpha\beta$-C_{32} %
E 48985	25.0	94.8	13.6
E 48986	25.3	101.2	13.6
E 48987	26.8	93.9	0.0
E 48988	16.7	271.4	6.8
E 48989	0.0	338.5	0.0